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A THEORETICAL AND EXPERIMENTAL STUDY OF THE LIME/LIMESTONE WET SCRUBBING PROCESS

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A THEORETICAL AND EXPERIMENTAL STUDY OF THE LIME/LIMESTONE WET SCRUBBING PROCESS

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ABSTRACT

This report describes results of Radian technical assistance to EPA in several areas concerning the development of the lime/limestone wet scrubbing process: (1) review of a portion of the test plan for EPA's Prototype Test Facility at TVA's Shawnee Station; (2) laboratory studies concerning key reaction steps, including lime and limestone dissolution rates and calcium sulfite and sulfate precipitation rates; (3) engineering and chemistry support for pilot unit studies at Combustion Engineering's Kreisinger Development Laboratory, including test program design, on-site sampling and chemical analysis of test samples at Radian, and engineering analysis of test results; and (4) chemical analysis support at Shawnee, including assistance with the analytical data system.

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1.0 SUMMARY

Under EPA Contract No. 68-02-0023, Radian provided technical assistance in several areas concerning the development of the lime/limestone wet scrubbing process: (1) review of Bechtel's preliminary test plan for EPA's test facility at TVA's Shawnee Station; (2) laboratory studies concerning key reaction steps; (3) engineering and chemistry support for pilot unit studies at Combustion Engineering's Kreisinger Development Laboratory; and (4) trouble-shooting at the analytical system at Shawnee.

1.1 Shawnee Test Plan Review

Radian reviewed the preliminary Shawnee test plan proposed by Bechtel in June 1971. The review was concentrated in the two month period of June - July 1971 and involved an in-depth examination of three Bechtel documents:

(1) Bechtel Corporation, "Alkali Scrubbing Test Facility - Screening Experiments for Venturi Scrubber System", Progress Report to APCO, Bechtel Corporation, San Francisco, May 1971.

(2) Bechtel Corporation, "Alkali Scrubbing Test Facility - Mathematical Models for Venturi Scrubber and After Scrubbers", Progress Report to APCO, Bechtel Corporation, San Francisco, February 1971.

(3) Bechtel Corporation, "Alkali Scrubbing Test Facility - Outline of Preliminary

Test Program for the Break-In Period", Report to APCO on Job No. 6955, Bechtel Corporation, San Francisco, May 1971.

Based upon its review of these documents, Radian's primary areas of concern were:

(1) The proposed test plan was a highly fractional factorial design. This design placed a strong dependence upon a good process model. The models proposed had several questionable assumptions.

(2) Even if the proposed model were correct, statistically significant conclusions would be very difficult from the number of experiments proposed. This is because neglected effects would mask the calculated effects.

(3) Further documentation of the test plan basis was needed in several key areas to establish its validity.

The test plan was modified somewhat to accommodate these criticisms.

1.2 Laboratory Rate Studies

Laboratory studies were conducted at Radian to measure: (1) the precipitation rates of calcium sulfate and sulfite; (2) the dissolution rates of lime and limestone; and (3) the solubility product constant for $CaSO_4 \cdot \frac{1}{2}H_2O$. Where possible, these results were correlated with process chemistry variables such as ion activities, amount and size of crystal seeds, and temperature.

Experimental measurements of $CaSO_4 \cdot 2H_2O$ precipitation rates support the following conclusions.

(1) A "metastable region" bounded by a relative saturation of 1.3 - 1.4 times the solubility product was observed. Below this level of supersaturation, precipitation occurs only on existing seed crystals. Above this level, nucleation begins.

(2) The precipitation rate of $CaSO_4 \cdot 2H_2O$ within the metastable region may be described by a rate expression of the form

$$R = k \cdot M \cdot (r-1) \qquad (1\text{-}1)$$

where R is the precipitation rate, k is the rate constant, M is a term dependent upon the amount of solid phase present, and r is the relative saturation.

For the seed crystal batches used in this study, the rate constant was correlated using the Arrhenius relation:

$$k\left(\frac{\text{g-moles}}{\text{g-min.}}\right) = 2.1 \pm .7 \times 10^{8} \exp(-9600/T) \qquad (1\text{-}2)$$

where T is measured in °K.

The kinetics behavior of $CaSO_3 \cdot \frac{1}{2}H_2O$ is qualitatively similar to that of $CaSO_4 \cdot 2H_2O$. Experimental results show that:

(1) The metastable limit for $CaSO_3 \cdot \frac{1}{2}H_2O$ nucleation is about three times the solubility product. Above this level of supersaturation, nucleation and dendritic growth occur on the surface of existing seed crystals. Scaling on equipment surfaces was also noted under these conditions. Pilot data seem to indicate that scrubbers may be operated free from calcium sulfite scale at super saturations above three. Thus calcium sulfite supersaturations of three would be a very conservative design basis.

(2) Within the metastable region, $CaSO_3 \cdot \frac{1}{2}H_2O$ precipitation is adequately described by the expression

$$R = k \cdot M \cdot (r-1) \qquad (1\text{-}1)$$

The rate was shown to be independent of changes in mass and area of growing crystals. For the seed crystals used in this study

$$k\left(\frac{\text{g-moles}}{\text{g-min.}}\right) = 7.3 \times 10^8 \exp(-10{,}600/T) \qquad (1\text{-}3)$$

where T is measured in °K.

Limestone dissolution rate experiments were conducted in dilute HCl solutions and simulated scrubbing liquors. In the dilute HCl test series, the following variable effects were noted.

(1) Limestone reactivity varied by as much as a factor of three for the four stones investigated.

(2) The temperature dependence of the dissolution rate corresponded to an Arrhenius activation energy of about 14,000 calories/g-mole.

(3) A significant agitation effect was seen at high and low levels of temperature and pH.

(4) The dissolution rate is approximately inversely proportional to particle size. The dissolution rate per unit of surface area is thus nearly constant.

These experimental observations indicate that limestone dissolution is probably limited by both surface phenomena and liquid film resistance. General correlation of results in this case would be particularly difficult.

Limestone dissolution rates in simulated scrubbing liquor could not be related to the dilute HCl test results in any consistent fashion. Experimental results for these tests showed that dissolution rates can be expected to be a strong function of pH. Soluble magnesium and chloride, on the other hand, do not appear to affect the dissolution rate in simulated scrubber liquor.

For purposes of process design estimates, the following guidelines may be used.

(1) Limestone dissolution rates in a hold tank environment (pH 6) should be on the order of 1×10^{-5} g-moles per minute per gram of limestone for 60 micron particles. The rate on a per gram of stone basis is inversely proportional to particle size.

(2) Limestone dissolution rates in a scrubber environment (pH 5) should be 30 to 40 times the hold tank rate. Thus significant limestone dissolution will occur in most scrubbers in spite of the low liquid hold up compared to that of a hold tank.

In view of the demonstrated complexity of limestone dissolution rate correlation, laboratory evaluation of candidate limestones is recommended as a standard design procedure. These tests should be conducted using a liquor typical of design operating conditions for the hold tank and scrubber environments.

Although the lime dissolution experiments did not successfully quantify the dissolution rate of lime in aqueous solutions, the following conclusion may be drawn from the qualitative results of this study:

(1) Subject to equilibrium constraints, lime particles of a given size will dissolve faster in aqueous solutions than limestone particles of the same size.

(2) This intrinsic rate difference is often enhanced by the fact that lime particles are typically smaller than limestone particles. This is particularly true of commercially prepared lime and limestone samples.

(3) Well-stirred process hold tanks containing solid phase hydrated lime can probably be assumed to be saturated with respect to $Ca(OH)_2$ in the liquid phase.

(4) The dissolution rate of a typical lime sample is so rapid that a significant contribution to the total alkalinity of the system can be expected to be supplied by lime species which initially enter a scrubber in the solid phase. The effects of this rapid dissolution rate should be taken into account whenever attempting to model or design a lime scrubbing system for SO_2 removal.

1.3 Pilot Unit Studies

Radian provided technical assistance during an EPA-sponsored pilot program on Combustion Engineering's 10,000 ACFM* marble-bed scrubber in Windsor, Connecticut. Radian's participation included test program design, on-site sampling and chemical analysis, chemical analysis of test samples at Radian, and engineering analysis of the test results. Key process rate steps were measured.

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* Engineering units in this report are expressed in English units. A list of conversion factors for determining metric equivalents is given in Section 8.2 of this report, page 185.

Three types of pilot tests were performed. First, scrubber performance was measured using sixteen experiments in which sodium carbonate was used as the alkali. Following these tests, six limestone injection/wet scrubbing tests were performed. Six limestone tail-end wet scrubbing tests were performed to conclude the EPA/CE/Radian pilot program.

The following conclusions were drawn from the results obtained in the soluble sodium carbonate tests:

(1) The liquor sampling and analytical techniques applied were adequate to investigate chemical processes occurring in soluble sodium carbonate/wet scrubbing systems.

(2) A vapor-liquid equilibrium approach of 95% can be obtained in single marble bed with a high pH sodium carbonate scrubbing liquor.

(3) Operating variables such as gas velocity and temperature do not appear to have a strong effect on the overall vapor-liquid mass transfer rate. This may indicate that the gas-film mass transfer rate does not limit the overall vapor-liquid mass transfer rate.

(4) The correlation between overall mass transfer rate and liquor pH exhibited in Figure 4-4 indicates that a liquid phase resistance is a substantial portion of the overall vapor-liquid mass transfer resistance.

From the results obtained in the limestone injection/wet scrubbing tests the following conclusions were drawn.

(1) The slurry sampling and analytical techniques applied in these tests adequately revealed the chemical processes occurring in limestone injection/wet scrubbing systems. Difficulty was encountered in characterizing the marble bed due to its non-uniform composition, however.

(2) Operating variables such as additive rate, flue gas flow rate, liquid to gas ratio, and liquor flow rate appear to affect the overall vapor-liquid mass transfer rate only through their effect on the operating pH of the marble bed. This correlation between vapor-liquid mass transfer and pH indicate that a liquid phase resistance is a significant portion of the overall vapor-liquid mass transfer rate.

(3) The precipitation rates observed in the limestone injection/wet scrubbing tests could be described by the same general form as the rate correlation observed in Radian laboratory research.

$$R = kM(r-1) \tag{1-1}$$

Therefore, circulation of large amounts of solids in the slurry increases the precipitation of and decreases the supersaturation of $CaSO_3$ and $CaSO_4$ in the scrubbing system. The magnitude of sulfite precipitation rate was considerably lower in the pilot unit than in the laboratory study, however. Sulfate precipitation rates were comparable.

(4) Over one-half of the system additive dissolution occurs in the scrubber in spite of low liquid residence times. The additive dissolution rate is apparently a strong function of liquor pH.

(5) Safe supersaturation limits for scale-free operation agree with those established in the laboratory for calcium sulfate (1.3 - 1.4), but appear to be higher for calcium sulfite. The limestone injection/wet scrubbing system operated in a scale-free condition with calcium sulfite supersaturations up to 6-8.

The data and calculations obtained for the six limestone tail-end addition/wet scrubbing tests support the following conclusions.

(1) The analytical and hold tank sampling methods employed were adequate for investigating important vapor-liquid and solid-liquid reaction rates in the process vessels. Poor results caused by marble bed sampling probe problems indicate the importance of very short sampling times.

(2) The amount of $CaSO_4 \cdot 2H_2O$ precipitation in the scrubber is always a substantial fraction of the total $CaSO_4 \cdot 2H_2O$ precipitation for the system (≈ 50%) in spite of the low liquid residence time in the marble bed. This is presumably due to high supersaturations and high nucleation rates in the marble beds. $CaSO_3 \cdot \frac{1}{2}H_2O$ precipitation in the marble bed is low, but significant (≈ 10%).

(3) Over 50% of the $CaCO_3$ dissolution in the wet scrubbing system occurs in the scrubber in spite of its relatively small liquid hold up. This is due to the high driving force for dissolution occurring in the marble beds. This is consistent with laboratory results showing a strong relationship between limestone dissolution

rate and pH. Limestone dissolution rates in the hold tank agree well with laboratory results.

(4) There are significant amounts of precipitation and dissolution occurring in the surge tanks which should be taken into account in pilot plant studies, and perhaps in process design.

(5) Vapor-liquid mass transfer rates are similar to those experienced in previous slurry and soluble test series. Their correlation with marble bed pH is again significant. It is also evident that there is a direct relationship between the vapor-liquid mass transfer rates and the number of marble beds. These facts indicate that SO_2 removal is limited by liquid phase mass transfer resistance and by interfacial area, not by the equilibrium partial pressure of SO_2.

(6) Increasing the total scrubber liquid-to-gas ratio decreases the sulfite supersaturation significantly but does not appear to affect the sulfate supersaturation.

One goal of the SO_2 scrubbing tests at Windsor was to gain experience in the characterization of processes that may be helpful during EPA's on-going prototype program at Shawnee.

Several aspects of the sampling and data interpretation procedures used at Windsor were discussed as to their relevance to the Shawnee tests. Other aspects, particularly those dependent on relative flow rates, vessel configurations, and modes of operation, would not be related. A major difficulty in relating the two programs was the differences in test goals and proposed data interpretation procedures.

1.4 Analytical Support for Shawnee

Analytical support for the Shawnee Alkali Scrubbing Test Facility involved several trips to Paducah to correct hardware and software problems in the Laboratory Analysis System.

1.5 Solubility Product of $CaSO_4 \cdot \frac{1}{2}H_2O$

In order to allow for a more complete and accurate mathematical description of the precipitation of calcium sulfate salts in lime/limestone wet scrubbing systems, the solubility of calcium sulfate hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) was investigated. Solubility data for calcium sulfate hemihydrate was collected from the literature and correlated. The following correlation form was selected:

$$-R \ln K_T = -81.826056 + 12.707705 \ln T + 3429.0616 T^{-1} + .054204619 T \qquad (1\text{-}4)$$

where R is the gas constant in calories/g-mole °K, K_T is the solubility product constant and T is the absolute temperature in °K. Equation (1-4) is based upon an investigation to to determine the optimum number of constants so as to result in a correlation form having the least number of terms but an error still in accordance with the accuracy of the experimental data.

2.0 INTRODUCTION

Limestone-based scrubbing processes are considered one of the most promising means of controlling sulfur dioxide and particulate emissions from fossil fuel-fired power plants. The Environmental Protection Agency has sponsored a number of research and development programs to accelerate the commercialization of limestone scrubbing processes for stack gas cleaning. They are presently conducting an extensive program to test a prototype lime/limestone scrubbing system at TVA's Shawnee generating station at Paducah, Kentucky with Bechtel as the primary engineering contractor.

Radian has been actively involved in EPA's lime/limestone scrubbing programs for the past four years. The work reported here represents the fourth major EPA-Radian contract. In Radian's first contract (CPA 22-69-138), a theoretical interpretation of the complex chemistry and chemical engineering aspects of lime/limestone scrubbing processes was developed. Under Contract No. CPA 70-45, Radian developed and exercised a process model of lime/limestone scrubbing processes such that the sensitivity of system performance to various process parameters was demonstrated. Radian also provided technical assistance to EPA in a series of pilot unit tests conducted at EPA's Cincinnati laboratories under the same contract. Under Contract No. CPA 70-143, Radian developed sampling and analytical chemistry techniques for determining the key chemical species in liquid and slurry streams of lime/limestone scrubbing processes. These methods are being used by TVA in the conduct of the Shawnee test program.

Under the present contract, Radian (1) reviewed the preliminary test plan proposed by Bechtel in June 1971 for the Shawnee program, (2) conducted laboratory studies to measure and correlate key reaction steps, (3) provided technical support in the conduct of pilot studies at Combustion Engineering's Kreisinger Development Laboratory, and (4) performed troubleshooting tasks to insure proper operation of the analytical system at Shawnee. Each of these task areas will be reported in a major section of this report.

3.0 REVIEW OF SHAWNEE TEST PLAN

EPA is currently conducting demonstration tests of the lime/limestone wet scrubbing process at TVA's Shawnee power plant at Paducah, Kentucky. The purpose of these tests is to demonstrate the operability and performance of lime/limestone scrubbing systems and to obtain valuable design data for commercial application of such systems. Bechtel Corporation was responsible for the design and construction of this alkali scrubbing test facility. In addition, Bechtel has primary responsibility for directing the test program, including the devising of an experimental plan which would effectively accomplished the program objectives. TVA was the constructor and is responsible for the operation of the test facility.

Radian as part of EPA Contract No. 68-02-0023 was responsible for reviewing a portion of the preliminary Shawnee test plan proposed by Bechtel, which was aimed at the development of mathematical models of the scrubbing facility. This section of the report will summarize the key aspects of Radian's review of the Bechtel test plan.

It should be noted here that Radian's review of the Shawnee test plan essentially involved an in-depth examination of three Bechtel documents:

(1) Bechtel Corporation, "Alkali Scrubbing Test Facility - Screening Experiments for Venturi Scrubber System", Progress Report to EPA, Bechtel Corporation, San Francisco, May 1971.

(2) Bechtel Corporation, "Alkali Scrubbing Test Facility - Mathematical Models for Venturi

Scrubber and After Scrubbers", Progress Report to EPA, Bechtel Corporation, San Francisco, February 1971.

(3) Bechtel Corporation, "Alkali Scrubbing Test Facility - Outline of Preliminary Test Program for the Break-In Period", Report to EPA on Job No. 6955, Bechtel Corporation, San Francisco, May 1971.

Radian's review was concentrated in the two month period of June-July 1971.

3.1 Background

The alkali scrubbing test facility at Shawnee consists of three parallel systems. These systems were designed to permit simultaneous testing of Venturi, Turbulent Contact Absorber (TCA), and Marble Bed (Hydro-Filter) scrubbers. A six month break-in period was proposed by Bechtel whereby each of the systems is operated to familiarize personnel with plant performance characteristics, define laboratory manpower requirements, and obtain some preliminary test data. Screening experiments on each of the scrubber systems were to follow the break-in experiments. The major goal of the screening experiments as stated by Bechtel was to obtain correlations of dependent variables such as SO_2 removal, particulate removal, and scrubber pressure drop with the independent variables of the scrubbing system. A set of primary experiments were to follow the screening experiments.

The test plan proposed by Bechtel for the screnning experiments using the Venturi scrubber system involved performing 80 experiments. The experimental plan was a statistically designed set of experiments using a fractional factorial design which was intended to allow for computation of all first-order effects and selected higher order effects.

Radian's review resulted in criticisms regarding both the statistical design utilized and the engineering aspects of the program. Radian's major comments in these two areas will be summarized below.

3.2 Statistical Approach

The Bechtel screening experiments were based on a fractional factorial experiment plan. The effects on a set of desired output (criterion) variables of a number of different factors were to be investigated simultaneously. Because of the complexity of the Venturi scrubber system, there are a large number of possibly significant independent variables (factors). To completely determine the interactions of the factors, a prohibitively large number of experiments would be necessary, even if only two levels are to be considered for each factor. A fractional factorial plan consists of performing only a portion of the total number of experiments necessary to completely determine the interactions.

The hazard of a fractional factorial test plan is that the results may easily be misinterpreted, especially if the process studied is not well understood. The results are obtained in the form of "effects" of the interactions of the independent variables. For a complete factorial design, a unique expression relates the experimental measurements of the criterion variable to each possible interaction of the factors. For a fractional replication, however, the same expression may be used to compute the estimate of several interaction effects. Those interactions which have the same effect expressions are said to be "aliases" of each other.

Interpretation of the experimental results is made possible by comparing expected interaction effects with a model of the process studied. If the total effect of the aliases of each significant interaction is known to be negligible, the experimental results can be unambiguously interpreted. Thus, effects in a fractional factorial experiment will be correctly attributed to specific interactions only if the following conditions are satisfied.

First, a model of the process studied must be exercised to predict values of interaction effects. The interactions with largest predicted effects are selected as the "significant interactions" to be tested. The fractional factorial experiment is then designed so that only "negligible" interactions are aliased with the significant interactions. If the sum of all aliased interaction effects is small compared with that significant interaction effect, the experimental results can be unambiguously interpreted. If the model is sufficiently accurate, the unambiguous interpretation will be correct.

The factorial experiment plan proposed by Bechtel involved thirteen two-level factors, one three-level factor, and one four-level factor, for a total of 98,304 possible combinations of factor levels. For the 80 experiment plan proposed, the fractionality is 80/98,304, or approximately 1/1200. This means that each measured interaction effect is aliased with about 1200 other interactions. A particular measured effect will therefore be the sum of the effects of 1200 aliased interactions. Interpretation of the effect as due to a particular interaction is based upon a process model predicting correctly the sum of 1199 effects is negligible compared with the 1200th interaction effect.

As may be seen from the above discussion, a highly fractional factorial experiment design must be based on an accurate process model if meaningful conclusions are to be expected. For portions of the process in which the mechanisms are in doubt, alternate plausible models should be developed. Significant interactions for alternate models should be computed and tested in a factorial experiment. This would tend both to decrease the masking of interaction effects and to provide a method for choosing between alternate models.

In summary, the test plan proposed by Bechtel was highly fractional. It was questionable whether the proposed mathematical model could be demonstrated to be a good representation of the physical system.

3.3 Engineering Aspects

In addition to the statistical points mentioned above, several comments concerning the major engineering aspects of the experimental plan are noteworthy. These comments are concerned with (1) choice of variables, (2) selection of experimental design, (3) ability to perform the proposed experiments, and (4) determination of model and its constants.

The proper choice of process variables is extremely critical to the success of any experimental program. On the one hand, all of the important variables must be included before correlation of the experimental data is possible. If a significant independent variable is omitted from the experimental design, any significant effect of this "hidden variable" will be attributed to other factors. Possible hidden variables in the proposed program include composition of the coal and limestone.

Bechtel had used a mathematical model to devise a statistical experiment plan. However, a number of steps were involved in selecting which interactions should be considered in the fractional factorial design. Bechtel formulated mathematical models. These models were then converted to test equations. The resulting set of test equations were then programmed on the computer. Simulation runs were performed using the "test equation" programs and the results of these simulation runs were analyzed to select the significant interactions in a "sum of effects" representation. Thus, the validity of experimental design depended not only upon the model assumptions, but it also depends upon the soundness of each of the steps described above.

In reviewing the mathematical models presented by Bechtel, it appeared they generally did a fairly complete treatment consistent with technology available at the time. One major discrepancy was their assumption of the vapor-liquid mass transfer rate being controlled by the gas-film resistance only. Experimental results from EPA's in-house experiments using a pilot Venturi scrubber (LO-027) indicate that liquid phase composition had a significant influence upon the v-ℓ mass transfer rate. This assumption was a serious limitation of the Bechtel model. Radian recommended the model be appropriately modified. A second area of Bechtel's mathematical model which was potentially weak was their treatment of solids dissolution and precipitation. Bechtel's treatment needed reexamination in three areas: (1) some of their assumptions were questionable, (2) several plausible models should be postulated and tested, and (3) additional details concerning their models were needed.

The ability to conduct the experiments required by the test plan is an important consideration. The process must be operable in each of the modes designated in the design. The independent variables must be controllable to a suitable level of precision and the desired quantities must be quantitatively measurable. Bechtel did not address these points in their screening experiments test plan. One potential difficulty in controlling significant variables involves the sequencing of experiments to treat different batches of additives and coals. Uncontrollable variations between batches could cause the independent variables to vary significantly. The test plan did not comment on this potential problem.

The Bechtel test plan involved performing 80 experiments to determine the effects of 15 independent variables. Test equations were developed to determine the significant interactions in the fractional factor design. These test equations involve 28 undetermined coefficients (β coefficients). Bechtel described a method of determining these β coefficients that are based upon considering "subsystems". The concept of determining coefficients in the model or test equations by dividing the process into its component parts and then making selected measurements is a good one from the standpoint of efficiency in constant determination.

However, a number of specific points concerning the manner in which Bechtel planned to determine constants was raised in the Radian review.

3.4 Summary

Bechtel proposed a set of 80 experiments based upon a fractional factorial design with 15 independent variables. Radian reviewed Bechtel's proposed test plan with respect to their statistical approach and with respect to the engineering aspects of their design. The following conclusions were drawn:

(1) The proper design of a highly fractional factorial experiment plan is based upon having a good understanding of the physical phenomena occurring within the process and expressing this in the form of a valid mathematical model. It was questionable whether this much faith should be placed in the model proposed by Bechtel.

(2) Interpretation of highly fractional factorial designs is extremely difficult because many interaction terms are aliased. It was questionable whether the proposed mathematical model could be demonstrated to be a good representation of the physical system based upon Bechtel's test plan for the Venturi screening experiments.

(3) The proper choice of process variables is extremely critical to the success of an experimental program. Bechtel's choice of variables could have resulted in some hidden variables and in some unnecessary interaction terms.

(4) The experimental design for "screening" experiments should examine all of the plausible models. Bechtel's design ignored the liquid-film resistance in v-ℓ mass transfer step and did not consider all aspects of s-ℓ mass transfer phenomena.

(5) Each of the steps in developing a fractional factorial design from a mathematical model is critical to the validity of the resulting design. Not enough information was available to properly evaluate the validity of these steps.

(6) The ability to conduct the experiments (operating modes, adequate variable control, and analytical measurements) required by the test plan is an important consideration. Bechtel did not specifically mention this point.

(7) One of the objectives of the proposed set of "screening" experiments is to determine test equation coefficients. Bechtel's method of subdividing the test equations system into component parts was not necessarily consistent with their test plan design.

(8) All plausible models should be considered in the interpretation of the experimental results. Analysis of variance techniques can be used to test hypotheses so that the proper model is selected.

It is important to note that the Bechtel test plan was subsequently modified, partly as a result of Radian's comments. The revised plan was reported by EPA at the Second International Lime/ Limestone Wet Scrubbing Symposium (EP-002). In addition, the current Shawnee test program places more emphasis on demonstration of reliable and economically attractive operating conditions.

4.0 LABORATORY RATE STUDIES

The rates of three solid-liquid reaction steps are known to be important in design and operation of lime or limestone wet scrubbing processes for SO_2 removal. These steps are (1) additive (lime or limestone) dissolution, (2) calcium sulfite precipitation, and (3) calcium sulfate precipitation. Quantitative prediction of process performance requires information relating the rates of these reactions to important process design parameters.

Laboratory investigation of the kinetics of these reactions was undertaken as a first step in developing a general process design technique. The objective of this study was to formulate a useful rate expression for each of these reactions.

4.1 Experimental Techniques

It is convenient to formulate a rate expression for solid-liquid mass transfer in terms of measurable process variables. A suitable rate expression may be written in the form of Equation 4-1.

$$R = k \cdot M \cdot \phi \qquad (4\text{-}1)$$

where R is the reaction rate of a given solid, k is a rate "constant" which may vary with liquor temperatures, composition, and transport parameters, M is a term dependent on the amount of solid phase present, and ϕ is some function of the actual and equilibrium concentration of the dissolving species. The typical experimental approach involves measurement of R at known or constant values of M and/or ϕ. The rate constant k is then calculated. Applicable parameters are varied over ranges expected to prevail in a typical process and the measured rates or rate constant correlated for use in large scale design.

The reaction rate, R, is most commonly determined by chemical analysis of the liquid phase to detect an increase or decrease in concentration of the dissolving or precipitating species. Alternately, the increase or decrease in weight of the solid phase may be measured. The "M" term is usually assumed to be proportional to the exposed surface area of the solid phase. This obviously may be difficult to quantify in experiments with suspensions of many fine particles. For dissolution and precipitation reactions, Ø is nearly always taken to be the difference between the actual and equilibrium concentrations of the reacting species, perhaps raised to some power.

In order to quantify R, M, and Ø, a means of contacting the two phases must be selected. Three categories generally considered are fixed-solid/moving-liquid, moving-solid/fixed-liquid (agitated only by the solid itself), and agitated-liquid/suspended-solid. The first two techniques are generally used in more fundamental studies where it is desirable to have quantitative descriptions of liquid velocity profiles and well defined surfaces for dissolution. Since the present study is intended for direct application to limestone scrubbing process design where agitated tanks will be used, only the third technique will be considered here. Quantitative application of data from flow situations other than an agitated suspension does not appear to be practical, given the present knowledge of phenomena involved.

There are at least three choices regarding experimental operation of an agitated vessel. These are as follows:

a. batch-liquid/batch-solid,
b. continuous-liquid/batch-solid,
c. continuous-liquid/continuous-solid.

The first of these is simplest from the operational standpoint but the most complex in terms of data analysis. A characterized batch of solids is introduced to a prepared solution and the concentration of the liquor monitored with time. For slow reactions, grab samples give adequate results. For faster rates, in-situ measurement using ion electrodes or conductivity is required. Calculation of the rate involves differentiation of the concentration versus time data as well as correction for any significant changes in area of the solids during an experiment. An additional complication can arise if the rate is both particle size and area dependent as happens in some cases.

The continuous-liquid/batch-solid method is very convenient for systems in which the change in the amount, area, and size of solids is negligible during an experiment. Under these conditions, a "steady state" material balance for the liquid phase gives the rate directly without differentiation of a concentration curve.

The third method is the most difficult to achieve experimentally since continuous addition of solids is necessary. It does, however, offer a true steady-state rate regardless of changes in the solid mass, area, and size. The rate is calculated directly from a steady state liquid or solid species balance.

For the present study, the continuous-liquid/batch-solid method was selected. Subsequent experiments proved successful for limestone dissolution and for calcium sulfite and sulfate precipitation. The selected apparatus and technique were not suitable for lime dissolution studies, however. A separate approach was taken using lime. This is described further in Section 4.5.

One problem addressed in the present investigation was design of an experimental apparatus permitting continuous liquid throughput while retaining a well-agitated suspension of small solid particles within the vessel. A successful method was eventually devised to retain even very fine solids in suspension during an experiment. A porous "Millipore" membrane was fixed across the reactor effluent port. A combination of a very large ratio of membrane area to reactor throughput and good agitation succeeded in preventing solids from accumulating on the membrane during a run. The flexibility and smoothness of the membrane contributed to the success of this technique since the agitation was sufficient to "ripple" its surface and dislodge any solids before a cake could form.

The final reactor configuration is shown in Figure 4-1. A single 142 millimeter membrane placed on a support screen fixed to the bottom of the reactor was used for liquid flow rates up to 400 milliliters/minute. For flows above this and for experiments using low agitator speeds, a second membrane was used at the top of the vessel.

The complete apparatus used to measure limestone dissolution and $CaSO_3 \cdot \frac{1}{2}H_2O$ or $CaSO_4 \cdot 2H_2O$ precipitation rates is shown schematically in Figure 4-2. Feed solutions are premixed in two separate 16 gallon polyethylene tanks. Na_2SO_3, Na_2SO_4, and $CaCl_2$ were used as sources of sulfite, sulfate, and calcium ions, respectively. $Mg(OH)_2$, $MgCl_2$, NaCl, HCl, and $Ca(OH)_2$ were also used to adjust the concentration of various species in the feed liquor. To prevent possible oxidation during sulfite experiments, deionized water was deaerated by nitrogen sparging before adding the reagents. The tanks were also fitted with floating lids to minimize oxidation of sulfite ion by atmospheric oxygen. The reactor was situated in a constant temperature bath

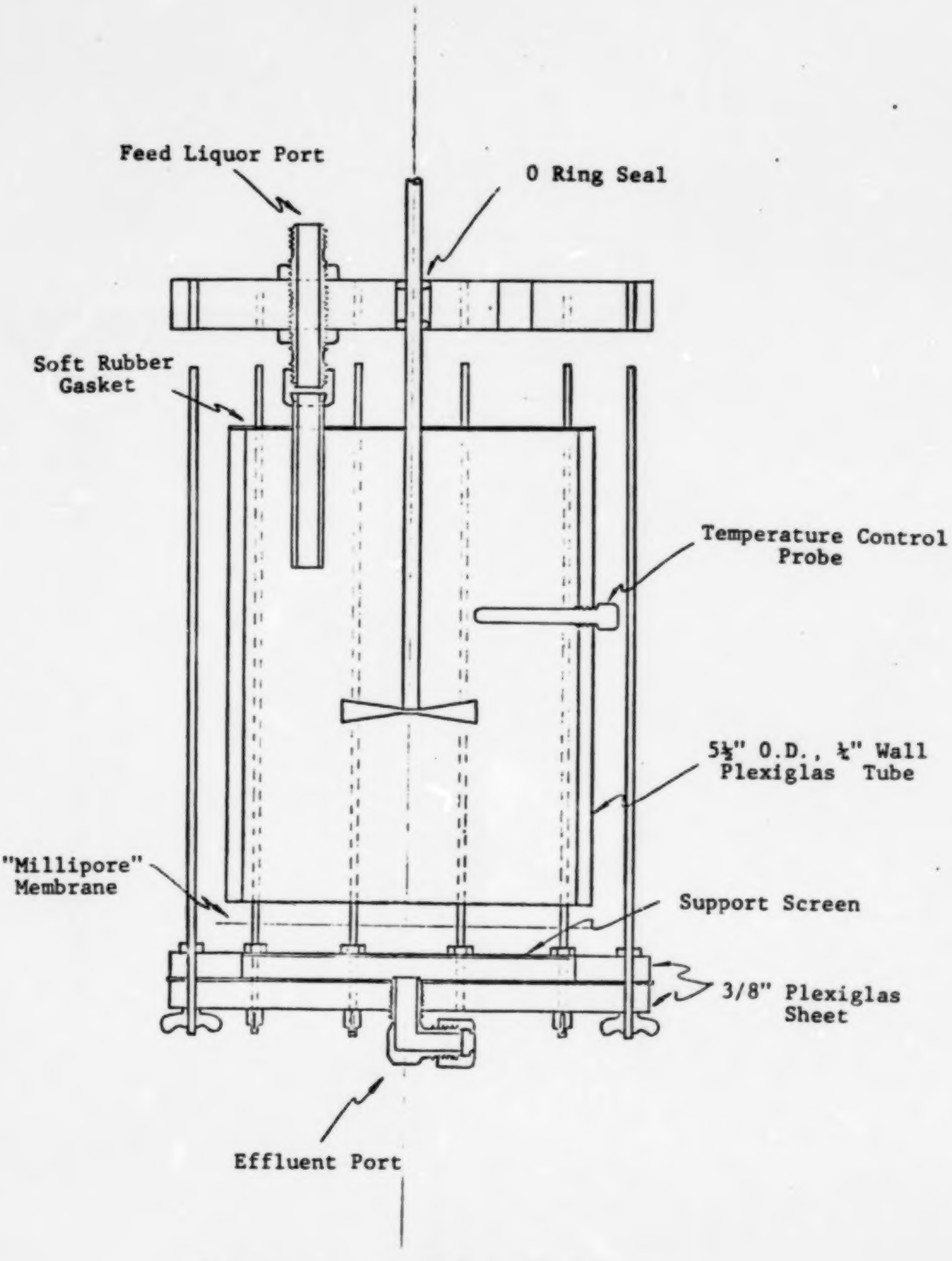
Feed Liquor Port
O Ring Seal
Soft Rubber Gasket
Temperature Control Probe
5½" O.D., ¼" Wall Plexiglas Tube
"Millipore" Membrane
Support Screen
3/8" Plexiglas Sheet
Effluent Port

FIGURE 4-1 - REACTOR CONFIGURATION

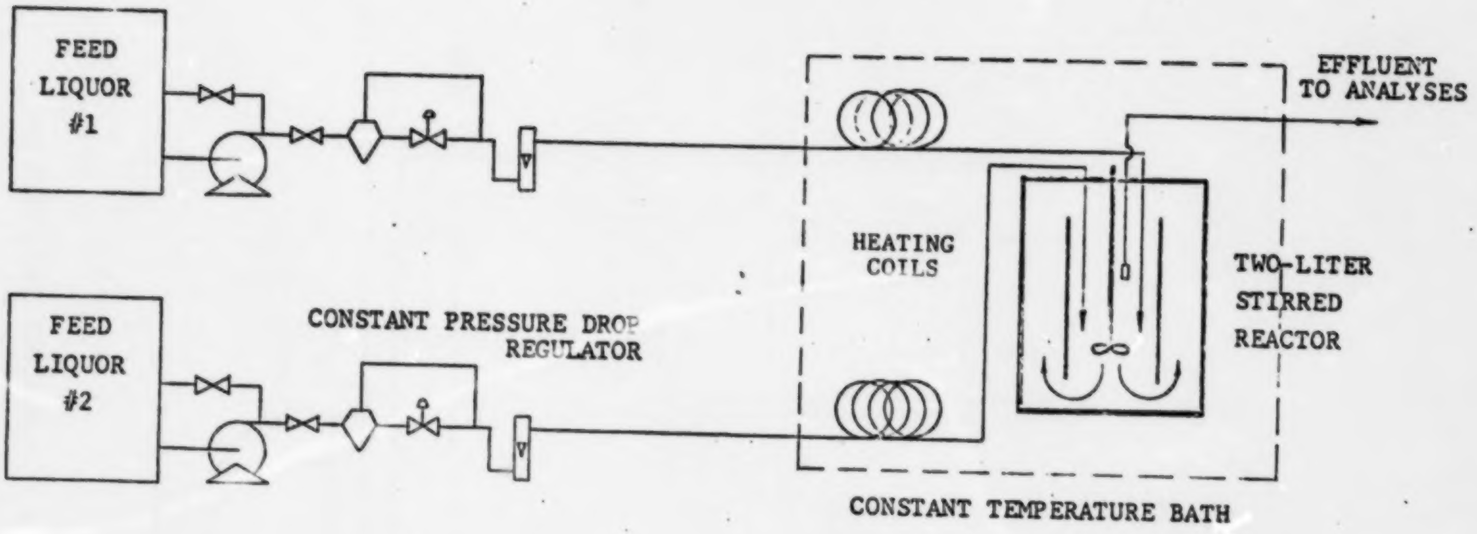
FEED LIQUOR #1
FEED LIQUOR #2
CONSTANT PRESSURE DROP REGULATOR
HEATING COILS
EFFLUENT TO ANALYSES
TWO-LITER STIRRED REACTOR
CONSTANT TEMPERATURE BATH

FIGURE 4-2
EXPERIMENTAL SYSTEM FOR PRECIPITATION RATE STUDY

and held at the desired experimental temperature by a controller powering a 750 watt immersion heater. Each feed solution was pumped through a separate train. Constant differential pressure flow controllers maintained selected flow rates through precision needle valves. The flows were measured by carefully calibrated rotameters. Both feed streams passed through about ten feet of 316 S.S. tubing in the bath before entering the reactor. The temperature within the vessel was held within about 0.5°C of the set point during a run.

Each experiment was initiated by introducing a known amount of solids to the reactor after it had been filled with feed solutions. The reactor was then closed and the feeds introduced as the desired flow rates. During a run, effluent samples were taken at intervals to evaluate whether steady state was reached. In most cases less than two residence times were required to approach the steady state reactor composition.

The "steady state" reaction rate for each experiment was calculated by straightforward material balance:

Reaction Rate (mole/min) = (4-2)

Feed Rate (ℓ/min) x Feed Concentration (mole/ℓ Ca or S)

- Effluent Rate (ℓ/min) x Effluent Concentration (mole/ℓ Ca or S)

An additional check was provided by a total solids material balance. The amount of product solids for a run is easily determined by emptying the reactor through the bottom port following shutdown so that the solids are retained on the effluent membrane. After air drying, the product cake is weighed and compared to the amount of solids introduced at start-up. The difference of these weights is the time integral of the reaction rate. This corresponds closely to the steady state rate multiplied by the total run time since the reaction was found to approach the steady state rate in a short period of time compared to the total run time.

4.2 $CaSO_4 \cdot 2H_2O$ Precipitation

Experimental results for the $CaSO_4 \cdot 2H_2O$ system have been summarized in Table 4-1. Calculated rates for the sulfate experiments are based on the total sulfur (total S) species balance in Runs 44-58 since the large excess of calcium introduces high uncertainty in the total calcium (total Ca) balance. An average of the total Ca and total S species balances was used for Runs 59-77.

Supersaturations for $CaSO_4 \cdot 2H_2$ were calculated using the chemical equilibrium computer routine developed under EPA contract CPA 22-69-138 and subsequently revised under contract CPA 70-45. The indicated relative supersaturations are ratios of the calculated ion activity products for each run divided by an equilibrium activity product calculated by inputting chemical analyses of an equilibrium solution of $CaSO_4 \cdot 2H_2O$ to the same computer routine. This method of calculation minimizes the effect of errors in the activity coefficient correlation used in the program. The "experimental" values of K_{sp} were $2.12x10^{-5}$, $2.15x10^{-5}$, and $2.19x10^{-5}$ at 45°, 40°, and 35°C respectively. These compare with values of 2.29, 2.34 and $2.38x10^{-5}$ used in the program originally.

The effects of experimental variables on precipitation rates are discussed below.

TABLE 4-1

EXPERIMENTAL RESULTS - PRECIPITATION OF $CaSO_4 \cdot 2H_2O$

Run No.	Amount of Seed (g)	Batch No.	$CaCl_2$		Na_2SO_4		Temp. (°C)	Stirrer Speed	Steady State Effluent Conc.◆ (mmole/ℓ)		Supersaturation	Precipitation Rate* (mmole/g-min)
			Feed Conc. (mmole/ℓ)	Flow Rate (ml/min)	Feed Conc. (mmole/ℓ)	Flow Rate (ml/min)			Ca	S	$\frac{a_{Ca^{++}} a_{SO_4^=} a_{H_2O}^2}{K_{sp}}$	
44	10.50	2	294	96	25.0	123	45	High	127	12.3	1.23	.036
47	10.55	"	288	"	41.0	"	"	"	124	14.5	1.41	.177
49	10.35	"	284	"	31.3	"	"	"	119	13.6	1.33	.084
50	10.47	"	284	"	36.2	"	"	"	119	14.3	1.39	.126
52	10.35	"	284	"	27.9	"	"	"	120	13.1	1.29	.054
53	10.39	"	284	"	41.5	"	"	"	116	14.7	1.38	.181
54	10.35	"	290	"	22.2	"	"	"	125	11.5	1.15	.020
55	10.38	"	271	"	24.5	"	"	"	120	12.3	1.22	.031
56	10.40	"	274	"	26.4	"	"	"	116	13.0	1.28	.038
57	10.36	"	274	"	26.7	"	"	"	118	13.2	1.30	.038
58	10.29	"	274	"	30.9	"	"	"	116	14.1	1.37	.069
59	10.25	3	56.2	97	45.8	"	"	"	23.0	23.5	1.22	.0415
61	10.26	"	61.1	"	48.8	"	"	"	24.2	24.0	1.26	.0645
62	10.31	"	63.2	"	50.7	"	"	"	25.0	24.1	1.27	.076
63	10.28	"	53.3	"	43.8	"	"	"	21.6	23.0	1.17	.0365
64	10.26	"	51.7	"	42.6	"	"	"	21.6	22.3	1.15	.0995
65	10.31	"	47.9	"	39.9	"	"	"	19.8	21.6	1.08	.0215
66	10.28	"	44.8	"	37.0	"	"	"	18.8	20.4	1.02	.013
71	10.23	"	53.2	"	45.8	"	"	"	23.1	23.2	1.21	.030
73	10.32	4	50.3	"	45.2	"	"	Low	21.0	23.2	1.15	.0345
74	20.60	"	50.2	"	44.5	"	"	High	20.0	22.5	1.09	.024
75	10.29	"	50.2	"	44.6	"	"	"	20.0	23.6	1.13	.034
76	10.26	"	49.7	"	46.1	"	35	"	21.1	24.4	1.24	.023
77	10.29	"	48.1	105	46.2	105	40	"	22.4	21.9	1.19	.029

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* Average of Total S + Ca balances were used in Runs 59-77. Total S balance only in Runs 44-58.

◆ S denotes total sulfur and Ca denotes total calcium.

4.2.1 Metastable Limit for Nucleation of $CaSO_4 \cdot 2H_2O$

Previous investigators have developed the concept of a metastable region for many crystal systems. This region is bounded by the solubility curve for a particular compound and a certain level of supersaturation below which crystal growth will occur but additional nuclei will not form. Since nucleation potential and scaling may be closely related, it is desirable to determine metastable limits for growth of $CaSO_4 \cdot 2H_2O$ seed crystals without nucleation.

Calculated precipitation rates for $CaSO_4 \cdot 2H_2O$ at the base temperature of 45°C have been plotted *versus* supersaturation in Figure 4-3. Photomicrographs comparing seed crystals with product crystals were used to detect the degree of formation of new crystals during a run. These photographs showed that the rapid rise in $CaSO_4 \cdot 2H_2O$ precipitation rates at relative supersaturations of 1.3-1.4 is due to nucleation. This is illustrated in Figures 4-4a through 4-4d.

4.2.2 Growth Rate Versus Supersaturation Within the Metastable Region

Various driving force functions have been proposed or used to correlate precipitation rates with supersaturation. Intuitively, it is clear that an adequate driving force function cannot be defined in terms of concentration of Ca^{++}, $SO_4^{=}$, or $SO_3^{=}$ in the solution. This follows from the fact that the thermodynamic solubility constant K_{sp} is a product of ion activities rather than concentrations. Thus, whether or not precipitation will occur (i.e., whether or not the driving force function is greater than zero) must be related to some comparison of the actual ion activity product to the solubility product. A function based on concentration would be valid only under conditions of

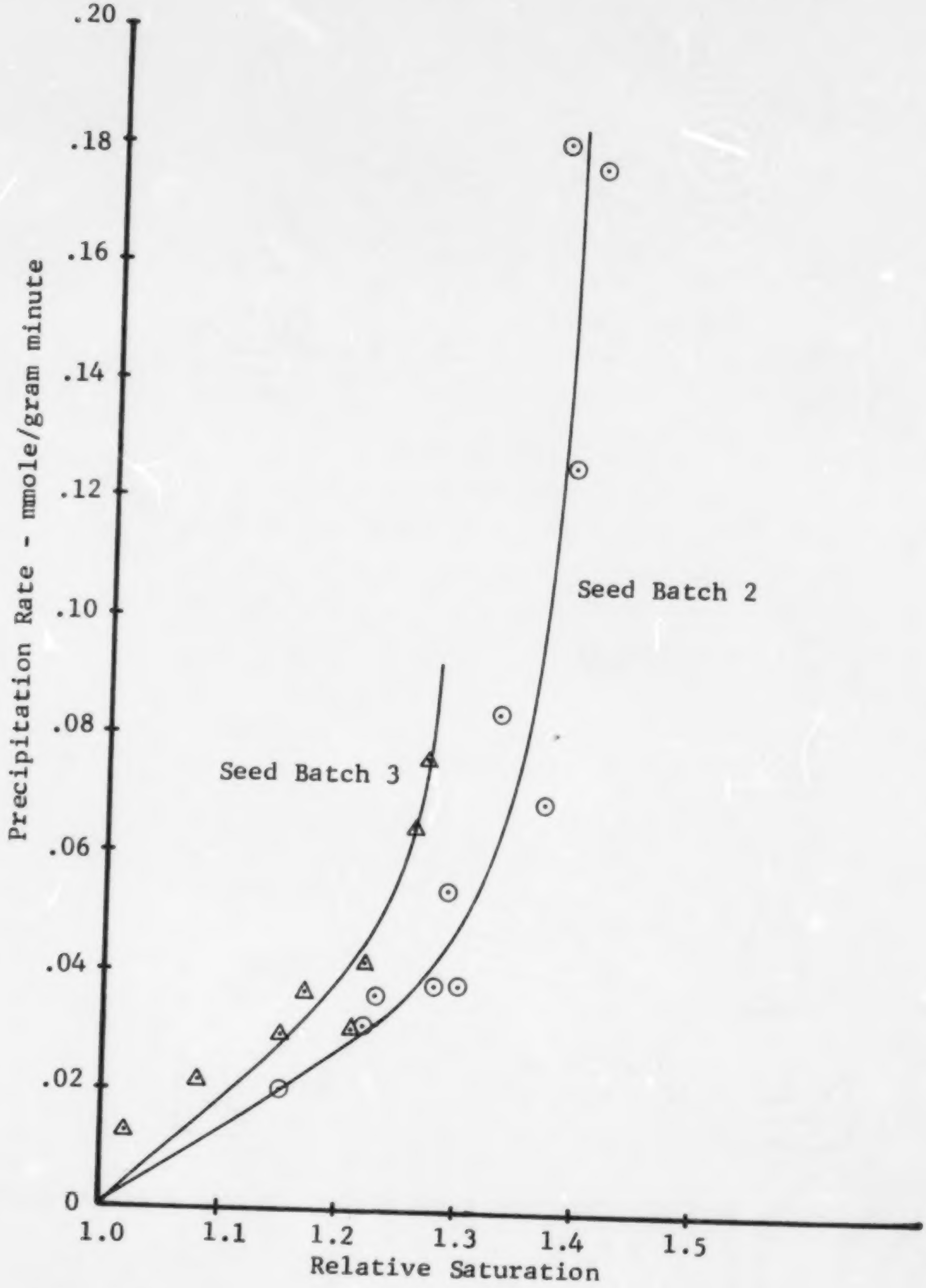
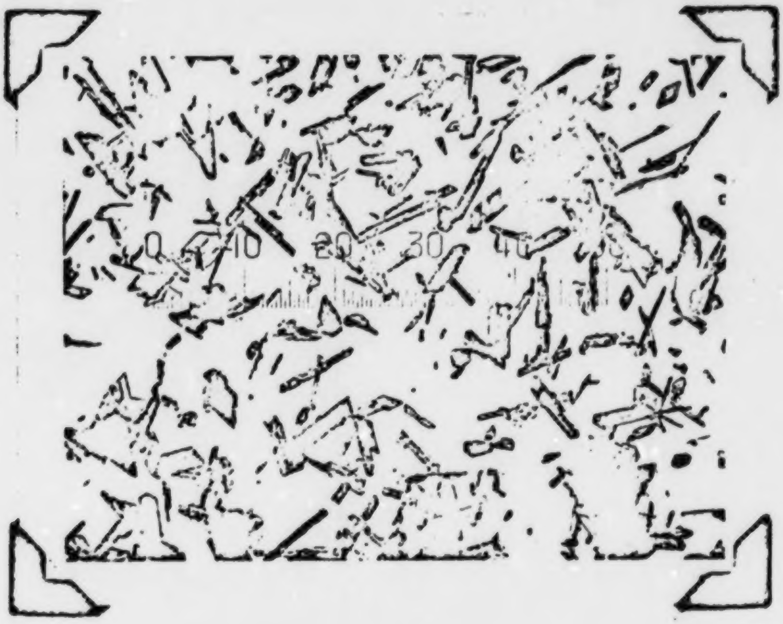


FIGURE 4-3 - $CaSO_4 \cdot 2H_2O$ PRECIPITATION RATE VERSUS RELATIVE SATURATION



0-50 = 500 Microns

FIGURE 4-4a

SEED CRYSTALS FOR $CaSO_4 \cdot 2H_2O$ PRECIPITATION EXPERIMENTS

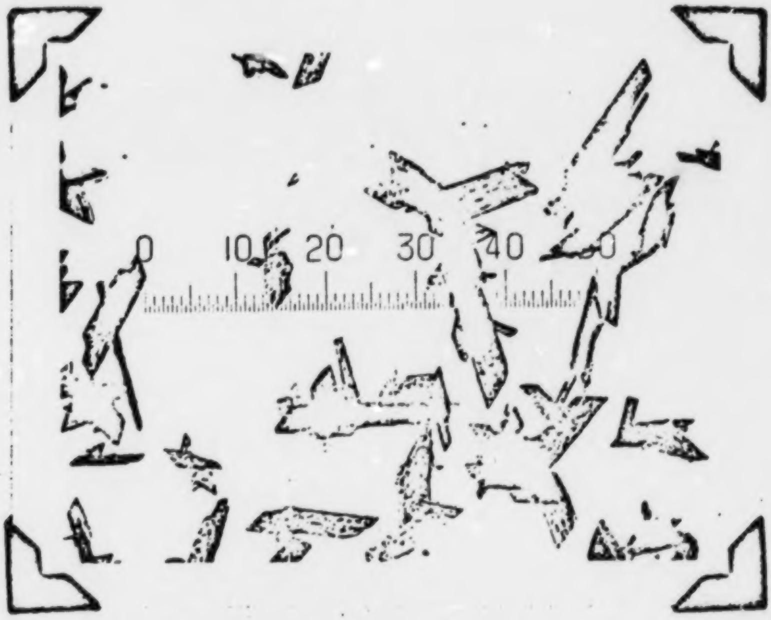

0
10
20
30
40
50

FIGURE 4-4b - PRODUCT CRYSTALS FROM RUN 66 AT LOW SUPERSATURATION ($1.02 \times K_{sp}$)

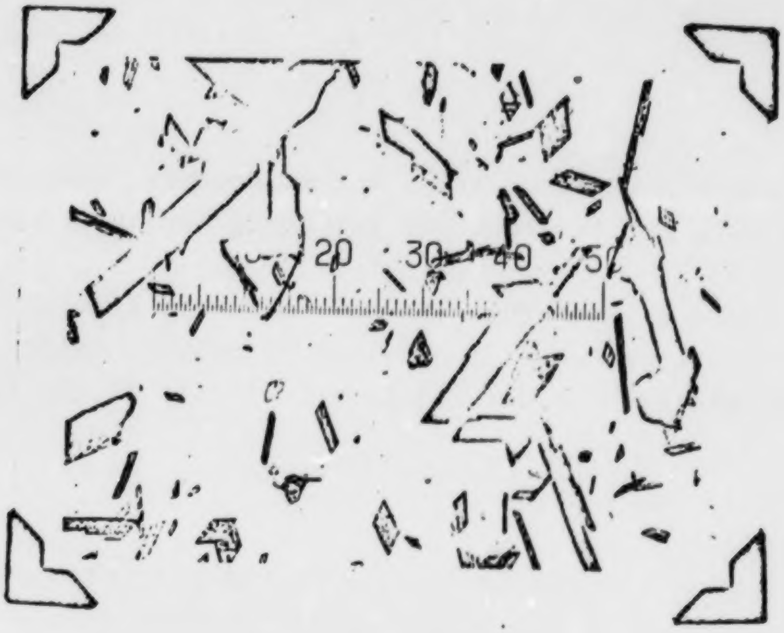
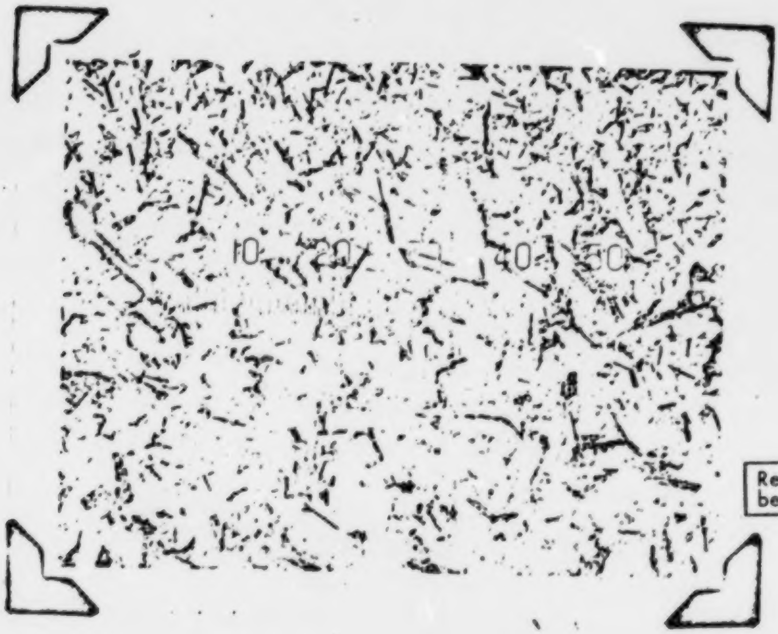


FIGURE 4-4c - PRODUCT CRYSTALS FROM RUN 62 AT INTERMEDIATE SUPERSATURATION ($1.27 \times K_{sp}$)



Reproduced from best available copy.

FIGURE 4-4d - PRODUCT CRYSTALS FROM RUN 53 AT HIGH SUPERSATURATION ($1.38 \times K_{sp}$)

constant ionic strength. It is known, however, that this is a major variable in limestone wet scrubbing applications.

Recent literature (NA-033) suggests that the precipitation kinetics of many slightly soluble ionic substances may be correlated by a driving force function of the form:

$$\emptyset = \left[\left(a_+^{n+} a_-^{n-}\right)^{1/n} - K_{sp}^{1/n}\right]^n \qquad (4\text{-}3)$$

Here, a_+ and a_- are the activities of the precipitating cation and anion, n_+ and n_- the number of cations and anions in the formula, and n the sum of n_+ and n_-. Thus, for $CaSO_4 \cdot 2H_2O$, Equation 4-3 becomes (assuming the activity of water is one):

$$\emptyset = \left[\left(a_{Ca^{++}} a_{SO_4^=}\right)^{\frac{1}{2}} - K_{sp}^{\frac{1}{2}}\right]^2 \qquad (4\text{-}4)$$

Figures 4-5 and 4-6 show plots of $CaSO_4 \cdot 2H_2O$ precipitation rate versus supersaturation. Two separate seed batches possibly having different size distributions were used for these runs so that each series must be considered independently. In each plot, a function of the form given in Equation 4-4 has been drawn through a reference datum. The reference run was selected on the basis of the best agreement between the total Ca and total S species balances for all the runs in each series. Also shown on each plot is a straight-line representation of the data fitting Equation 4-5.

$$\emptyset = a_{Ca^{++}} a_{SO_4^=} - K_{sp} \qquad (4\text{-}5)$$

Since the $CaSO_4 \cdot 2H_2O$ experiments were conducted at relatively low supersaturations, the data are somewhat scattered. Qualitatively, the linear driving force appears to offer a

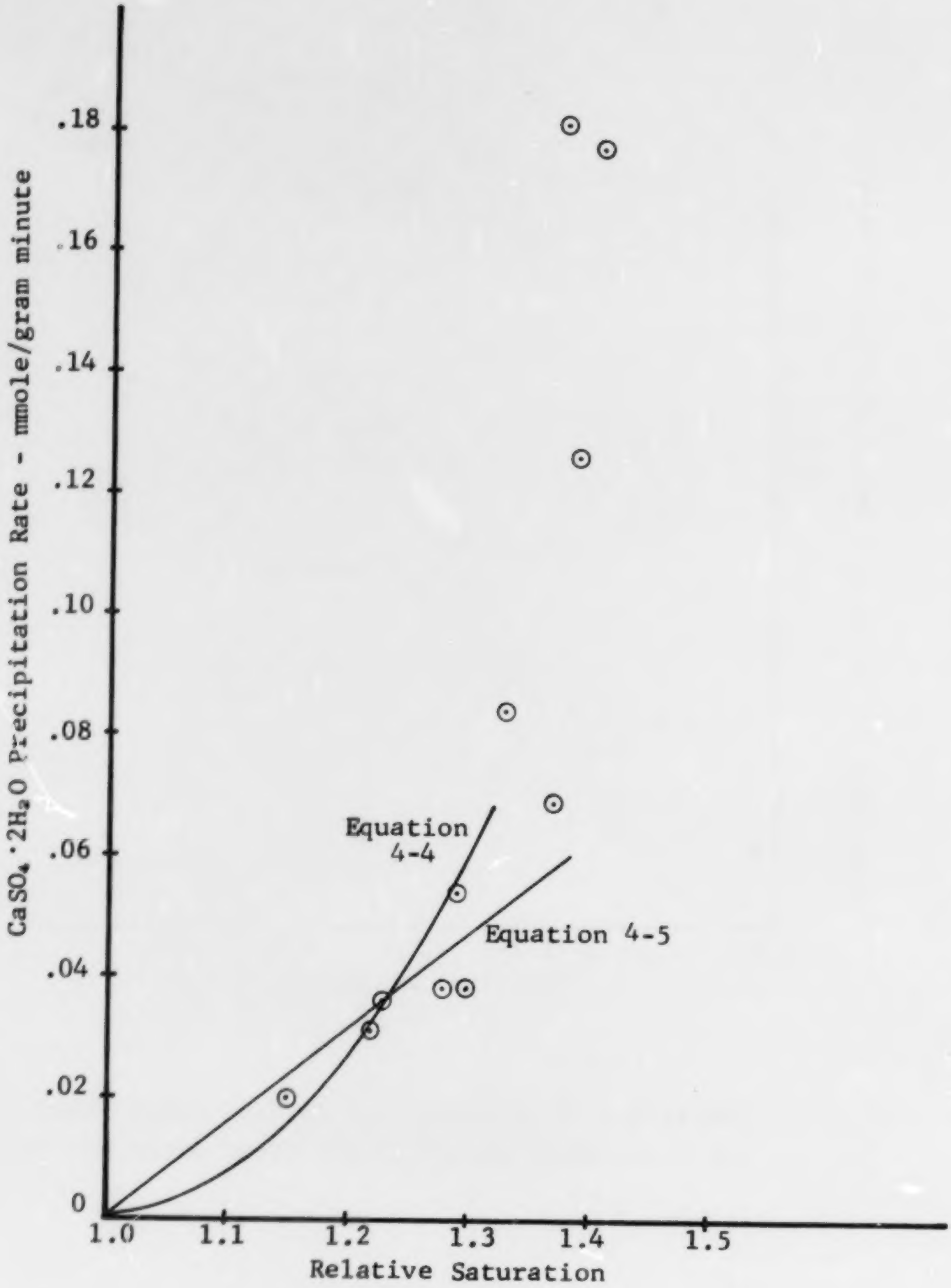


FIGURE 4-5 - COMPARISON OF HYPOTHESIZED DRIVING FORCE FORMS FOR $CaSO_4 \cdot 2H_2O$ PRECIPITATION (Seed Batch No. 2)

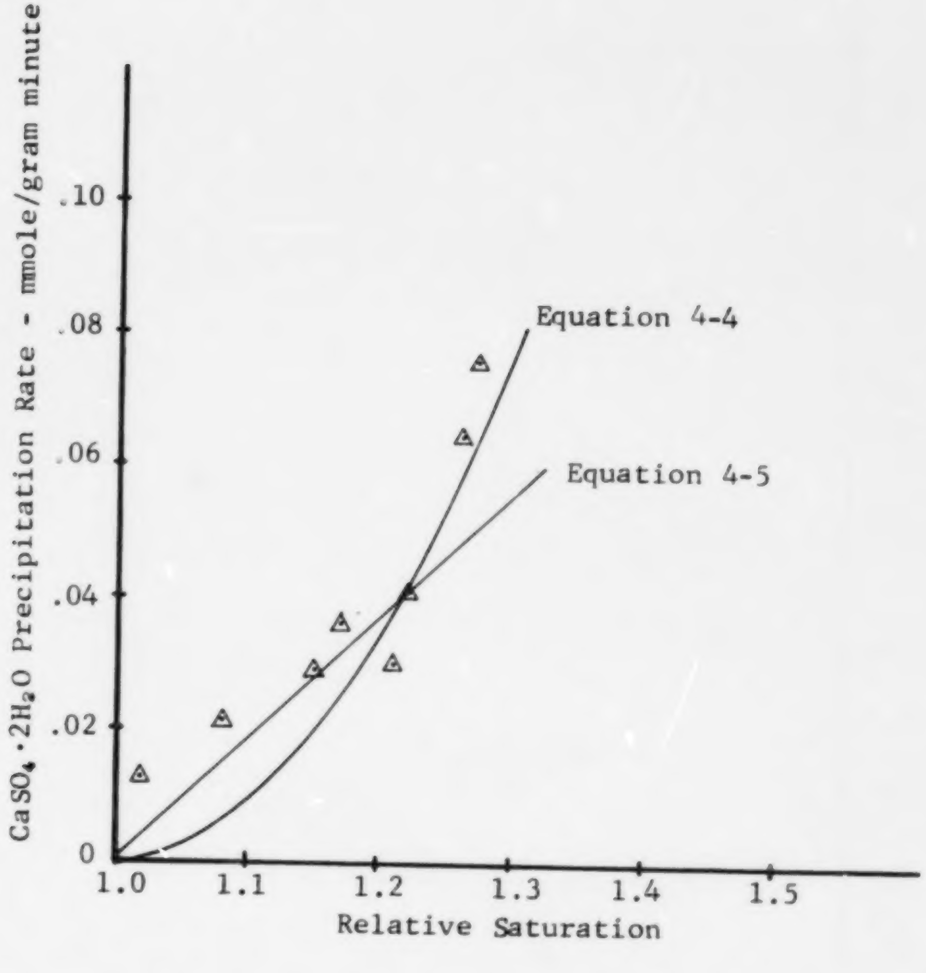


FIGURE 4-6 - COMPARISON OF HYPOTHESIZED DRIVING FORCE FORMS FOR $CaSO_4 \cdot 2H_2O$ PRECIPITATION (Seed Batch No. 3)

better representation of the data at lower supersaturations. The quadratic form follows the observed increase in precipitation rate at higher supersaturations, but this curvature is probably due to incipient nucleation rather than crystal growth. Therefore, Equation 4-5 is a good representation of the precipitation rate.

4.2.3 Effects of Temperature on $CaSO_4 \cdot 2H_2O$ Growth Rate

Definite temperature effects on precipitation rate were observed with both the sulfite and sulfate systems. Temperature effects on chemical reaction rate constants are normally correlated using the Arrhenius relationship

$$k = A \exp (E^*/RT) \qquad (4\text{-}6)$$

where k is the rate "constant", A a temperature independent constant, E* the so-called activation energy for the reaction, R the gas constant, and T the absolute temperature. Temperature effects for the $CaSO_4 \cdot 2H_2O$ system were investigated in a series of runs using a new seed batch. These data are shown in Figure 4-7. For purposes of estimating an activation energy, precipitation rates are assumed to be linear with relative supersaturation. Calculations using the 45°C and 40°C plots result in $E^* = 20.5$ kcal/gmole. The 40°C and 35°C comparison shows $E^* \cong 17.5$ kcal/gmole for an average of about 19 kcal/mole. A value of 15.0 kcal/mole for E* of $CaSO_4 \cdot 2H_2O$ was reported in a recent study by Liu (LI-012).

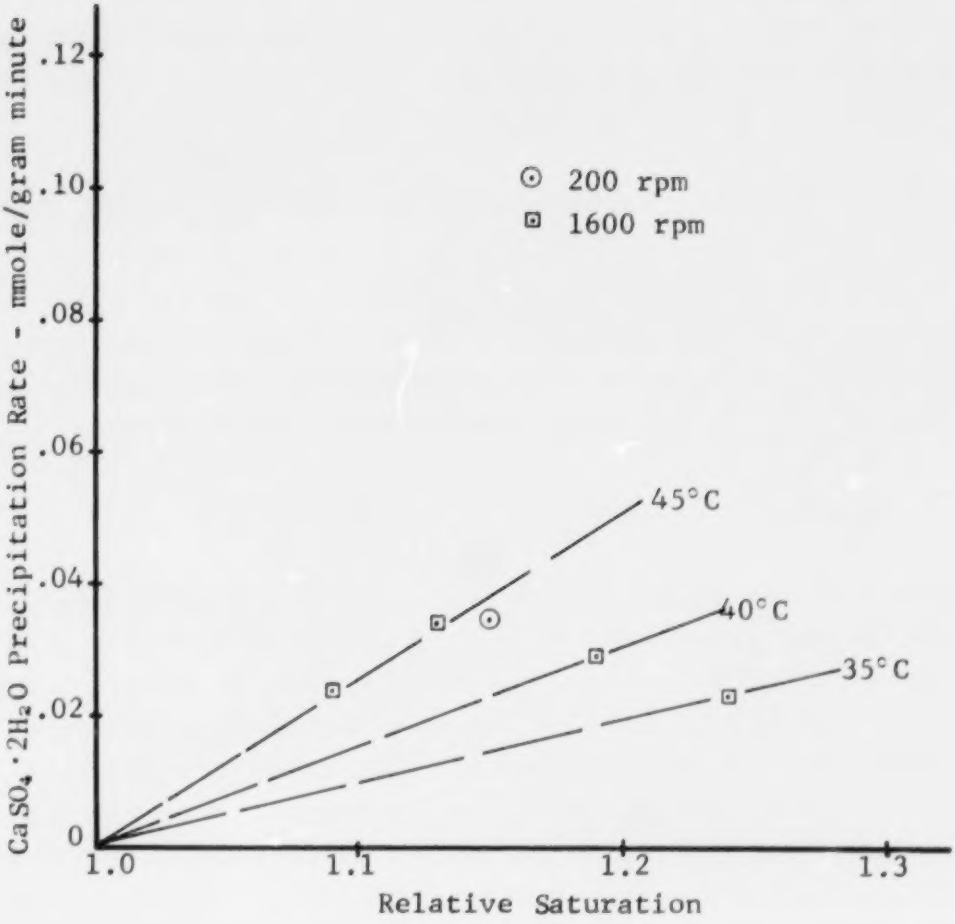


FIGURE 4-7 - EFFECT OF TEMPERATURE AND AGITATION ON $CaSO_4 \cdot 2H_2O$ PRECIPITATION RATE

4.2.4 Agitation Effects

Nearly all of the precipitation experiments were conducted with a high level of mixing in the reactor. In order to screen for possible effects of agitation on the rates, a run was conducted for each system at a stirring speed of about 200 rpm compared to the normal 1600 rpm. This low level was just sufficient to maintain a good seed suspension in the vessel.

Results for the $CaSO_4 \cdot 2H_2O$ system were shown on the previous plot (Figure 4-7). The difference in precipitation rate between the 200 rpm and 1600 rpm runs at 45°C does not appear to be significant.

4.2.5 Dependence of Precipitation Rate on Amount of Seed

With reference to the expression for the precipitation rate given in Equation 4-1, the dependence of the rate on the amount of seed crystal remains to be quantified. Experiments demonstrating the effect of the initial amount of seed in the reactor do not provide a complete description of the seed-dependent term in the rate expression. This procedure does not demonstrate whether the rate is proportional to the number, area, or mass of seed crystals. The rates of many two-phase chemical reactions have been assumed to be directly proportional to surface area, but some hypothetical mechanisms for crystallization do not necessarily lead to this conclusion. The dislocation theory of crystal growth, for example, hypothesizes that growth occurs by addition of ion pairs at the ends of screw dislocations, the number of which may remain constant as the area of a growing crystal increases.

One method of distinguishing between number, area, or mass-proportional rate mechanisms is to conduct an experiment during which the amount of crystal precipitated is substantial compared to the amount of initial seed. Under these circumstances, the present experimental procedure will result in a steady state reactor concentration only if the rate is proportional to the number of seed crystals rather than the area or mass.

Quantitative interpretation of these observations is not straightforward. While the effluent concentration of the reactants should change with time if the rate is area dependent, the magnitude of this effect is not readily estimated. The fact that the rate decreases significantly with concentration could tend to offset an increase due to an area change, making the net result difficult to detect. Also, the lag time inherent in a continuous stirred tank reactor (CSTR) would lessen the rate of change of the effluent concentration. In order to derive a conclusion regarding crystal growth rate versus surface area, a computer routine was written to approximate an unsteady state material balance for the reactor.

The material balance for a well-stirred vessel with reaction is given by

$$V \frac{dC}{dt} = F\left(C_{in} - C\right) - R(C) \qquad (4\text{-}7)$$

where C is the concentration of the reactant of interest, C_{in} is the initial concentration, V the volume of the vessel, F the flow rate, and R(C) the reaction rate (rate of precipitation). For known initial conditions, C(t) can be estimated using

$$C(t + \Delta t) = C(t) + \frac{F}{V}\left[C_{in} - C(t)\right]\Delta t - \frac{R(C)}{V}\Delta t \qquad (4\text{-}8)$$

For each successive time increment a new value of C(t) is calculated using a precipitation rate R(C) evaluated at the previous increment. For purposes of this calculation the precipitation driving force given by Equation 4-5 in terms of individual ion activities was reformulated in terms of concentration:

$$R(C) = k A_0 (\overline{\gamma}^2 C^2 - K_{sp}) \qquad (4\text{-}9)$$

The factor $\overline{\gamma}^2$ was established as a function of C so that

$$\overline{\gamma}^2 C^2 = a_{Ca^{++}} a_{SO_4^=} \qquad (4\text{-}10)$$

over the range of concentrations experienced. This was done so that the complete individual ion activity calculation need not be executed at each time increment in the calculation.

The product k A_0 was calculated from the experimental precipitation rate. During a computer simulation of the reactor, this product could either be held constant or increased according to the increasing area of the seed crystals to compare hypothesized rate forms.

Numerical results for growth of $CaSO_4 \cdot 2H_2O$ showed that the expected change in reactor effluent concentration versus time caused by an increase in seed area was within the accuracy of analytical techniques used. This is a consequence of operation near saturation. Even a small percentage change in composition in this region represents a large change in precipitation driving force. Thus, no conclusive evidence regarding the size dependence of $CaSO_4 \cdot 2H_2O$ growth rates could be obtained with the present experimental method.

4.2.6 Conclusions

Experimental measurements of $CaSO_4 \cdot 2H_2O$ precipitation rates support the following conclusions.

- A "metastable region" bounded by a relative saturation of 1.3 - 1.4 times the solubility product was observed. Below this level of supersaturation, precipitation occurs only on existing seed crystals. Above this level, nucleation begins. This phenomenon was verified in the Windsor pilot unit studies (see Section 5.4.4).

- The precipitation of $CaSO_4 \cdot 2H_2O$ within the metastable region may be described by a rate expression of the form

$$\text{Rate (g-mole/min)} = k \cdot M \cdot (r-1)$$

where k (g-mole/gram minute) is a temperature dependent rate constant, M (grams) is the mass of seed crystals, and r is the relative saturation defined by the ratio of the activity product and solubility product for the precipitating species. For the seed crystal batches used in this study the rate constant was

$$k \text{ (g-mole/gram-minute)} = 1.4\text{-}2.8 \times 10^9 \exp -(E^*/RT)$$

where: E^* = 19,000 calories/g-mole,
R = 1.98 calories/g-mole $^{\circ}$K,
T = temperature, $^{\circ}$K.

The smaller seed crystals in Batches 3 and 4 provided a higher reactivity per unit weight than those of Batch 2.

4.3 $CaSO_3 \cdot \frac{1}{2}H_2O$ Precipitation

A series of experiments similar to those described in Sections 4.1 and 4.2, was carried out using calcium sulfite seed crystals. $CaSO_3 \cdot \frac{1}{2}H_2O$ is the other major precipitating species of interest in limestone scrubbing processes. In general, the kinetic behavior was similar to the $CaSO_4 \cdot 2H_2O$ system. Experimental results are summarized in Table 4-2. All of the sulfite precipitation rates except Runs 13, 14, and 20 are an average of the total Ca and total S calculations. No unreasonable differences between these two values were noted. Important variable effects are discussed below.

4.3.1 Metastable Limit for Nucleation of $CaSO_3 \cdot \frac{1}{2}H_2O$

Figure 4-8 is a plot of experimental $CaSO_3 \cdot \frac{1}{2}H_2O$ precipitation rates *versus* relative saturation. A very rapid increase in rate occurs at a supersaturation of about three times the solubility product. Photomicrographs of seed and product crystals from runs at various supersaturations were again compared.

Figures 4-9a, b and c are photomicrographs of $CaSO_3 \cdot \frac{1}{2}H_2O$ seed and product crystals from Run 18 at a supersaturation (2.71) below the sharp increase in the rate curve and Run 15 at a supersaturation (3.55) above the increase in the rate curve. These again show that the seed crystals experience regular growth below a certain critical level of supersaturation but that nucleation predominates

TABLE 4-2

EXPERIMENTAL RESULTS - PRECIPITATION OF $CaSO_3 \cdot \frac{1}{2}H_2O$

Run No.	Amount of Seed (g)	$CaCl_2$ Feed Conc. (mmole/ℓ)	Feed Flow Rate (ml/min)	Na_2SO_3 Feed Conc.◆ (mmole/ℓ) SO_3	Na_2SO_3 Feed Conc.◆ (mmole/ℓ) SO_4	Temp. (°C)	Stirrer Speed	Steady State Effluent Conc.◆ (mmole/ℓ) Ca	Steady State Effluent Conc.◆ (mmole/ℓ) SO_3	Steady State Effluent Conc.◆ (mmole/ℓ) SO_4	Supersaturation $\frac{a_{Ca^{++}} a_{SO_3^{=}} a_{H_2O}^{1/2}}{K_{s,p}}$	Precipitation Rate** (mmole/g-min)
7	10.26	5.42	125	5.58	0.52	45	high	1.19	0.94	*	1.69	0.041
10	10.35	6.36	"	6.35	0.76	"	"	1.17	1.14	0.42	1.91	.048
13	10.27	*	"	13.7	----	"	"	1.93	1.32	.39	2.68	.125
14	10.25	*	"	18.85	0.30	"	"	1.79	1.62	.11	2.92	.191
15	1.00	9.96	"	12.25	----	"	"	1.54	2.35	.01	3.55	.901
16	"	7.92	"	7.54	0.16	"	"	1.85	1.64	.09	3.34	.529
17	"	5.85	"	5.82	----	"	"	1.80	1.49	.14	3.14	.301
18	"	4.10	"	3.81	0.15	"	"	1.63	1.28	.15	2.71	.121
20	"	4.04	"	*	*	50	"	1.59	1.09	.21	2.26	.108
21	"	4.51	"	4.19	0.22	40	"	1.67	1.41	.20	3.06	.147
22	"	36.4	"	35.7	2.0	45	"	15.9	14.9	2.0	2.63/3.95	.531
25	"	38.0	"	36.5	2.6	"	"	14.2	13.9	1.1	4.35	1.17
28	"	4.17	"	3.69	0.41	"	low	1.64	1.18	0.47	2.51	.106

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* Analysis not made.

** Average of total sulfur and total calcium balances.

◆ SO_3 denotes total sulfite sulfur, SO_4 denotes total sulfate sulfur, and Ca denotes total calcium.

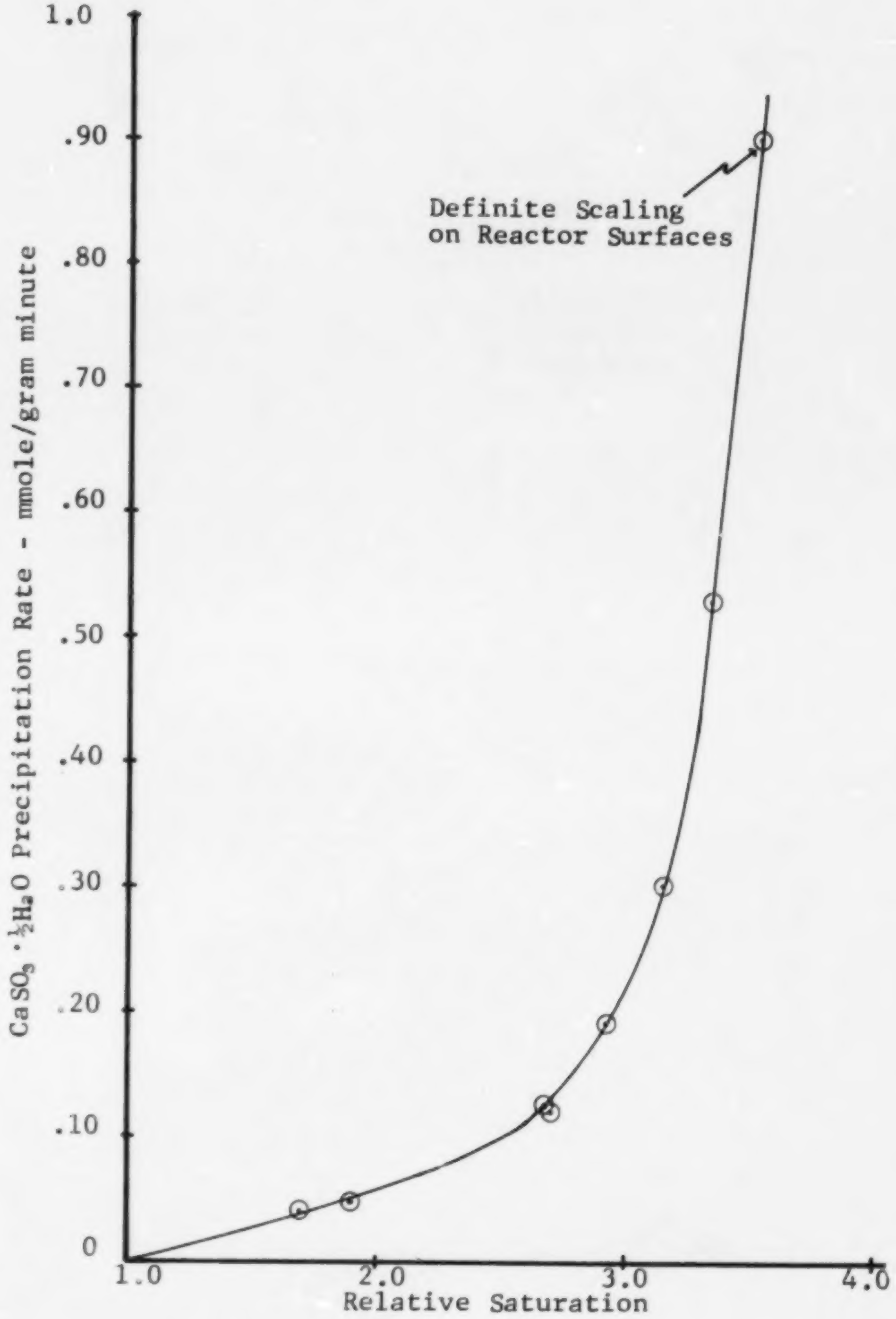

FIGURE 4-8 - $CaSO_3 \cdot \frac{1}{2}H_2O$ PRECIPITATION RATE VERSUS RELATIVE SATURATION

FIGURE 4-9a CaSO$_3 \cdot \frac{1}{2}$H$_2$O SEED CRYSTALS
0-50 = 500 µ

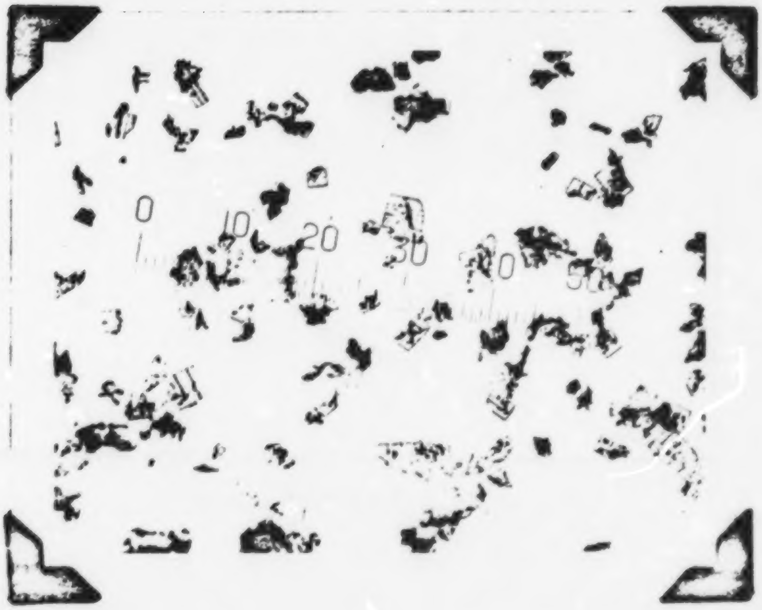
0
10
20
30
40
50

FIGURE 4-9b PRODUCT CRYSTALS FROM RUN 18
AT LOW SUPERSATURATION (2.71 x K_{sp})
0-50 = 500µ

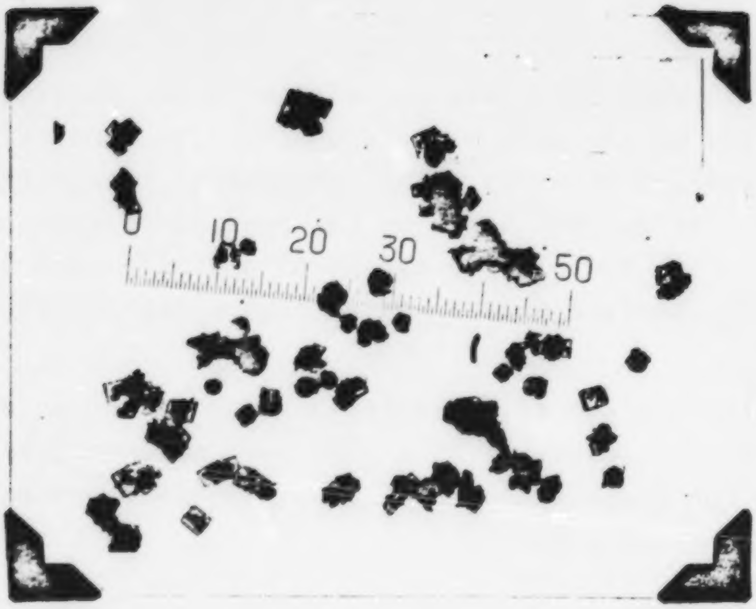

FIGURE 4-9c PRODUCT CRYSTALS FROM RUN 15 AT HIGH SUPERSATURATION (3.55 x K_{sp}) 0-50 = 500μ

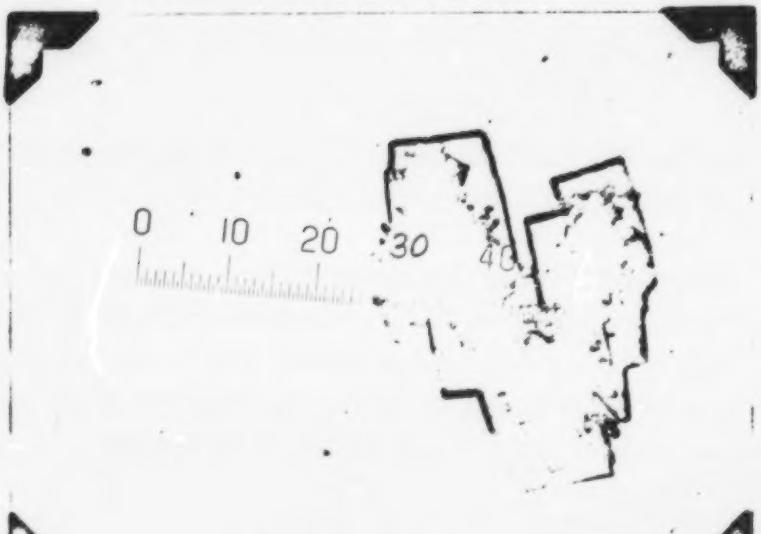

FIGURE 4-9d PRODUCT CRYSTAL FROM RUN 15 SHOWING SURFACE NUCLEATION ON SEED 0-50 = 125μ

above this level. Note that nucleation in the $CaSO_3 \cdot \frac{1}{2}H_2O$ occurs as formation of new growth sites on the seed surfaces rather than new smaller crystals. This phenomenon is easily seen in Figure 4-9c as dark areas on the previously translucent seed. Figure 4-9d is a photograph of a single seed crystal cluster with surface nucleation at higher magnification.

During Run 15, definite scaling was noted on all surfaces of the reactor. This scale was particularly adherent to the 316 S.S. material and to a lesser extent to the Plexiglas surfaces.

In summary, the $CaSO_3 \cdot \frac{1}{2}H_2O$ results showed that the seed crystals experience regular growth below a certain critical level of supersaturation but that nucleation predominates above this level. Nucleation of $CaSO_3 \cdot \frac{1}{2}H_2O$ occurs as formation of new growth sites on the existing seed surfaces rather than new smaller crystals as in the case of $CaSO_4 \cdot 2H_2O$.

4.3.2 $CaSO_3 \cdot \frac{1}{2}H_2O$ Growth Rate Versus Supersaturation Within the Metastable Region

The experimentally observed precipitation rates for $CaSO_3 \cdot \frac{1}{2}H_2O$ are compared with hypothesized driving force expressions in Figure 4-10. As in the $CaSO_4 \cdot 2H_2O$ comparison, the curves were driven through a datum having the best agreement between total sulfur and total calcium balances.

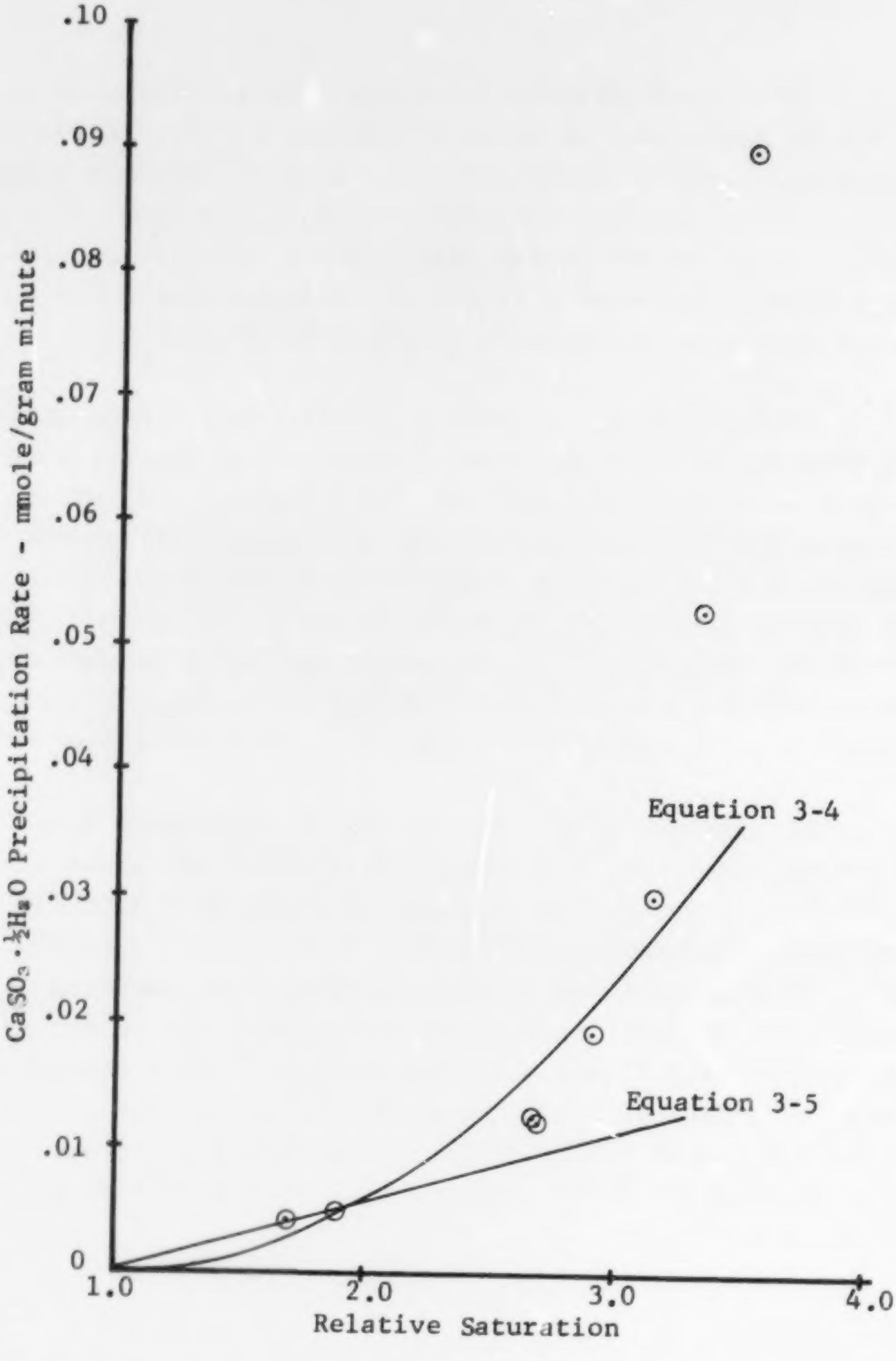

FIGURE 4-10 - COMPARISON OF HYPOTHESIZED DRIVING FORCE FORMS FOR $CaSO_3 \cdot \frac{1}{2}H_2O$ PRECIPITATION

The linear driving force function as indicated by Equation 4-5 is again seen to offer a somewhat better fit for data at low supersaturation. Neither form is adequate above a relative supersaturation of about 3.0 where nucleation becomes significant. The observed curvature in the rate above a relative supersaturation of about 2.5 probably is due to an increasing contribution from nucleation in addition to simple crystal growth.

Because of the bisulfite-sulfite equilibrium shift, calculated values of $CaSO_3$ supersaturation can be extremely pH sensitive in acid regions. For this reason, most of the experimental investigation of $CaSO_3 \cdot \frac{1}{2}H_2O$ precipitation was conducted in slightly alkaline liquors where nearly all of the total sulfite (total SO_2) in solution was in the form of $SO_3^=$. To check the validity of the observed rate curve in more acid regions, two runs were conducted at low pH levels. The pH of the reactor was adjusted by adding HCl to the $CaCl_2$ feed solution.

Figure 4-11 shows the results of these acid runs. Two data points bracketing the neutral rate curve are given for Run 22. These correspond to a measured pH range of 4.9 to 5.1 during this experiment and demonstrate the sensitivity of calculated sulfite saturations to pH variations. An improved technique for determining the reactor pH was used in Run 25. A constant pH of 5.22 was observed throughout this experiment. The resulting data point is reasonably close to the neutral solution rate curve. The driving force function and activity calculations appear to extrapolate well over a wide range of liquor compositions.

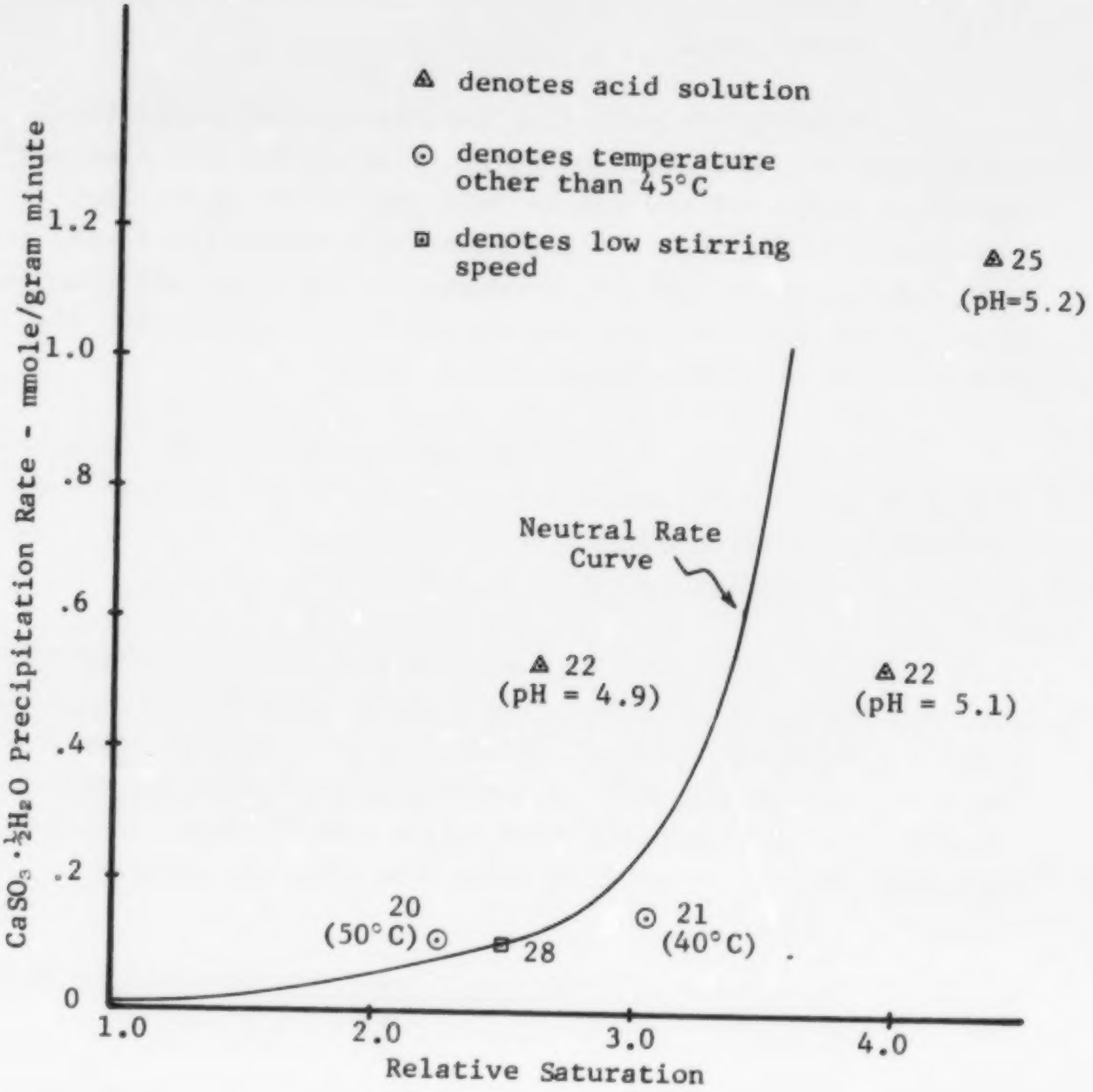

FIGURE 4-11 - EFFECTS OF pH, TEMPERATURE, AND AGITATION ON $CaSO_3 \cdot \frac{1}{2}H_2O$ PRECIPITATION RATE

4.3.3 Effects of Temperature and Agitation on $CaSO_3 \cdot \frac{1}{2}H_2O$ Growth Rate

Results of $CaSO_3 \cdot \frac{1}{2}H_2O$ experiments at temperatures other than 45°C and at a low level of agitation are also presented in Table 4-2 and Figure 4-11. As in the $CaSO_4 \cdot 2H_2O$ experiments there was no significant agitation effect with the $CaSO_3 \cdot \frac{1}{2}H_2O$ system. Run 28, conducted at 45°C and 200 rpm, was shown in Figure 4-11. Its rate is identical to the 1600 rpm 45°C rate curve within experimental error.

Temperature effects are again significant. Comparison of Run 20 at 50°C to the 45°C rate gives $E^* \cong 19.8$ kcal/gmole. A similar calculation with Run 21 at 40°C gives $E^* \cong 22.5$ kcal/gmole for an average of about 21 kcal/gmole.

The relatively high estimated activation energies and absence of agitation effects for both the sulfite and sulfate systems indicate a chemical reaction limited rather than a diffusion limited mechanism. A conservatively estimated mass transfer coefficient using literature correlations indicates a diffusion rate at least four times the observed rate.

4.3.4 Dependence of $CaSO_3 \cdot \frac{1}{2}H_2O$ Precipitation Rate on Amount of Seed

As discussed in Section 4.2, a growth rate dependence on crystal size or area should result in a change in reactor effluent concentration with time. Although this change was estimated to be below analytical detection for the sulfate experiments, it is significant for the sulfite data since these experiments were conducted at much higher relative saturations.

Runs 13 and 14 of the $CaSO_3 \cdot \frac{1}{2}H_2O$ series were conducted over periods of 75 minutes during which the mass of the seed crystals in the reactor increased by factors of about 2.3 and 2.8, respectively. This corresponds to an increase in seed area of about 75% for Run 13 and 100% for Run 14. In spite of this, the reactor effluent composition appeared to be constant with time, indicating that the rate is apparently independent of total surface area for a given batch of seed.

Figure 4-12 shows the results of computer simulations for the crystallizer based on conditions for Run 14. For the steady state case, the rate constant was held constant. For the unsteady state case, it was increased in proportion to the area of the growing crystals.

These numerical results show that the reactor effluent composition would decrease about 15% over the period from 15 minutes to 75 minutes during a run if the rate were proportional to the seed area. A decrease of this magnitude should be easily detected. No such decrease was observed during Run 14. Thus, the growth rate of $CaSO_3 \cdot \frac{1}{2}H_2O$ seed crystals appear to be independent of surface area.

4.3.5 Conclusions

The kinetics behavior of $CaSO_3 \cdot \frac{1}{2}H_2O$ is qualitatively similar to that of $CaSO_4 \cdot 2H_2O$. Experimental results show that:

- the metastable limit for $CaSO_3 \cdot \frac{1}{2}H_2O$ nucleation is about three or four times the solubility product. Above this level of supersaturation, nucleation and dendritic growth occur on the

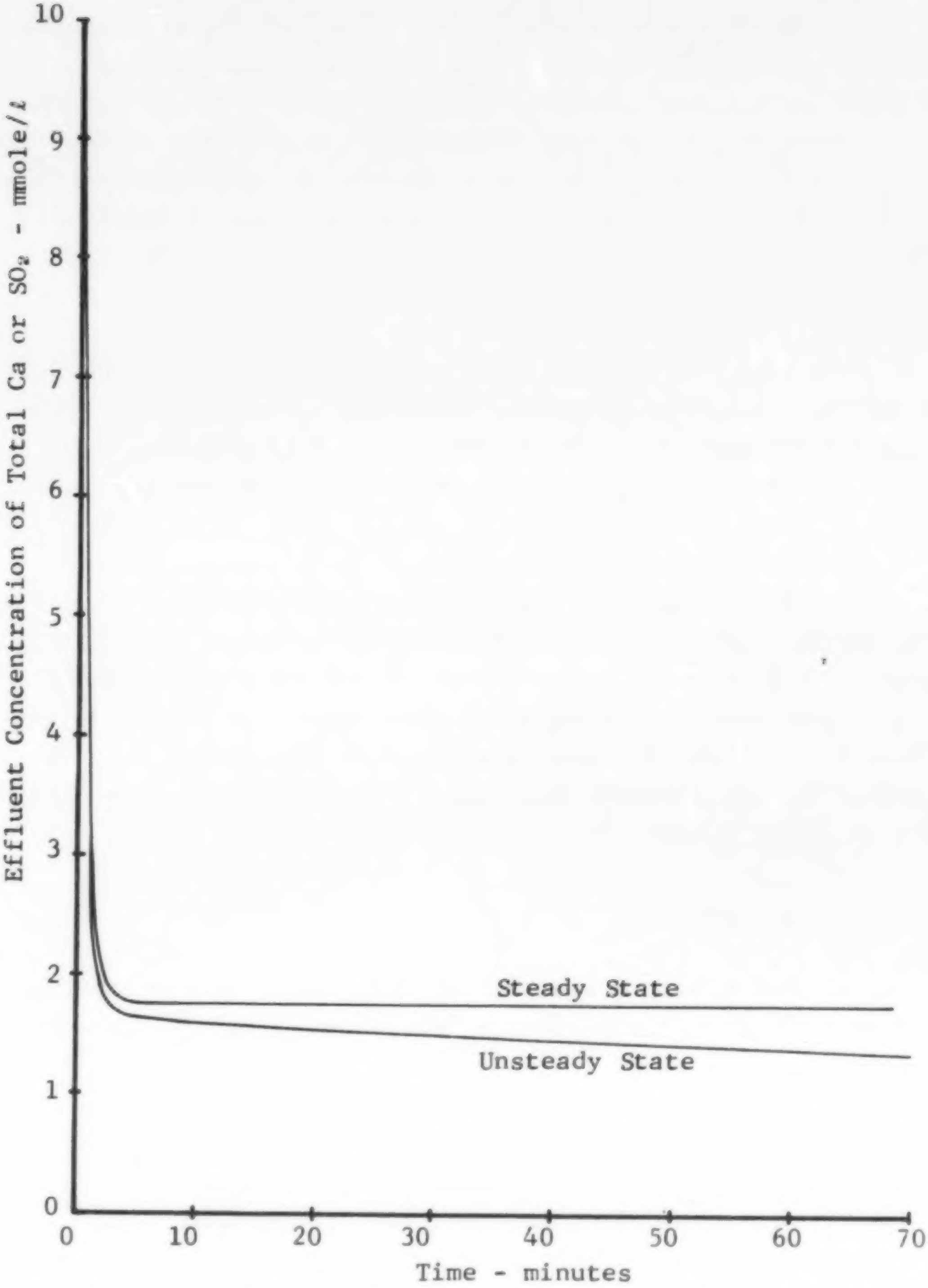

FIGURE 4-12 - NUMERICAL APPROXIMATION OF REACTOR COMPOSITION FOR RUN 14

surface of existing seed crystals. Scaling on equipment surfaces was also noted under these conditions. This phenomenon was not substantiated during the Windsor pilot tests (see Section 5.4.4).

- within the metastable region, $CaSO_3 \cdot \frac{1}{2}H_2O$ precipitation is adequately described by the expression

$$\text{Rate (g-mole/min)} = k \cdot M_0 \cdot (r-1)$$

where k (g-mole/gram minute) is a temperature-dependent rate constant, M_0 (grams) the initial mass of seed crystals, and r is the relative saturation as previously defined. The rate was shown to be independent of changes in mass and area of growing crystals. For the seed crystals used in this study

$$k \text{ (g-mole/gram-minute)} = 7.3 \times 10^8 \exp(-E^*/RT)$$

where $E^* = 21{,}000$ calories/g-mole.

4.4 Limestone Dissolution

A literature review conducted prior to this experimental study (see Radian Technical Note 200-014-07 in Appendix B of this report) suggested that a kinetic expression describing limestone dissolution under conditions typical of a limestone scrubbing system could be quite complex. The dissolution rate behavior of a solid which reacts with the solvent liquor can be a strong function of liquor composition. Not only can the overall rate vary markedly with liquor composition, but the dissolution mechanism or rate limiting step may also change.

Two basic series of limestone dissolution experiments were completed. The initial group of tests used simple dilute HCl solutions as the feed liquor. Effects of temperature, agitation, pH, limestone type, and particle size were screened. The second test series used synthetic liquors typical of those encountered in a closed-loop limestone scrubbing operation. Dissolution rates more suitable for design application were obtained in these experiments.

4.4.1 Limestone Dissolution in Dilute HCl Solutions

Results of dissolution experiments using dilute HCl feed solutions are summarized in Table 4-3. These runs covered a pH range from 4.9 to 8.6. Important experimental parameters shown in this table are explained briefly below.

> Limestone Type - Four different limestone types were used during the HCl test series. Types 1 and 2 were locally available high-calcium limestones. Types 3 and 4 were obtained from Dr. D. C. Drehmel of EPA. Type 3 is a hard calcite and 4 a soft marl. The petrographic and chemical characteristics of these stones were described by Drehmel in

TABLE 4-3

EXPERIMENTAL RESULTS - LIMESTONE DISSOLUTION IN DILUTE HCl SOLUTIONS

Run No.	Temp. (°C)	Limestone		Approx. Mean Particle Size (microns)	Stirrer Speed (RPM)	Feed Flow (ml/min)	HCl Conc. (mmoles/ℓ)	Effluent Concentration* (mmole/ℓ)			Activity (mmole/ℓ)		Relative Saturation $\frac{a_{Ca^{++}}a_{CO_3^=}}{K_{sp}}$	Dissolution Rate (mmole/g-min)	Fraction of Sample Dissolved at 3τ	Equilibrium Activity (mmole/ℓ)		Equilibrium Solubility (mmole/ℓ)
		Type	Wt. (g)					pH	Ca	CO_3	Ca^{++}	$CO_3^=$				Ca^{++}	$CO_3^=$	
14	50	1	5	60	~1000	400	0.500	6.50	.365	.262	.313	3.41×10^{-5}	6.6×10^{-3}	.029	.04	.42	4.3×10^{-3}	.51
15	50	1	5	60	~1000	400	0.500	6.70	.346	.293	.305	6.92×10^{-5}	1.1×10^{-2}	.028	.04	.42	4.3×10^{-3}	.51
16	50	1	5	60	~1000	400	0.790	6.35	.463	.395	.387	2.93×10^{-5}	6.2×10^{-3}	.037	.06	.62	2.9×10^{-3}	.78
17	50	1	5	60	~1000	400	0.790	6.30	.449	.401	.376	2.51×10^{-5}	5.2×10^{-3}	.036	.05	.62	2.9×10^{-3}	.78
18	25	1	5	60	~1000	400	0.380	6.05	.239	.259	.212	4.63×10^{-6}	2.0×10^{-4}	.019	.03	.34	1.3×10^{-2}	.40
19	25	1	5	60	~1000	400	0.380	6.05	.245	.278	.217	4.74×10^{-6}	2.1×10^{-4}	.020	.03	.34	1.3×10^{-2}	.40
20	50	2	5	60	~1000	400	0.240	7.65	.245	.269	.214	7.49×10^{-4}	8.8×10^{-2}	.020	.03	.24	7.6×10^{-3}	.28
21	50	2	5	60	~1000	400	0.240	7.80	.204	.241	.180	9.96×10^{-4}	9.9×10^{-2}	.016	.02	.24	7.6×10^{-3}	.28
23	27	3	5	60	1000	400	0.247	6.40	.204	.246	.182	1.58×10^{-5}	6.4×10^{-4}	.0165	.02	.245	1.8×10^{-2}	.29
24	27	3	5	60	850	400	0.247	6.00	.167	.251	.151	3.80×10^{-6}	1.3×10^{-4}	.0135	.02	.245	1.8×10^{-2}	.29
25	48	3	5	60	1000	400	0.207	8.25	.221	.247	.193	2.78×10^{-3}	3.0×10^{-1}	.0175	.03	.218	8.25×10^{-3}	.26
27	50	3	5	60	1000	400	0.193	7.45	.225	.279	.198	4.79×10^{-4}	5.2×10^{-2}	.018	.03	.210	8.60×10^{-3}	.24
28	49	3	5	60	850	400	0.193	7.10	.206	.229	.182	1.62×10^{-4}	1.6×10^{-2}	.0165	.02	.210	8.60×10^{-3}	.24
29	50	4	5	60	1130	400	0.199	8.60	.237	.253	.205	6.27×10^{-3}	7.1×10^{-1}	.019	.03	.213	8.45×10^{-3}	.25
30	26	4	5	60	1130	400	0.199	8.50	.237	.302	.208	4.29×10^{-3}	1.9×10^{-1}	.019	.03	.213	2.06×10^{-2}	.25
32	50	4	2	60	1130	400	0.341	6.30	.251	.216	.220	1.45×10^{-5}	1.8×10^{-3}	.050	.07	.307	5.90×10^{-3}	.36
33	50	4	2	60	815	400	0.341	5.70	.206	.126	.183	8.68×10^{-7}	8.8×10^{-5}	.041	.06	.307	5.90×10^{-3}	.36
35	50	2	10	60	1100	200	8.50	5.04	4.01	4.13	2.51	1.62×10^{-6}	2.25×10^{-3}	.080	.24	3.42	5.28×10^{-4}	6.16
36	50	2	10	60	1100	100	8.56	5.22	4.18	4.19	2.59	3.65×10^{-6}	5.24×10^{-3}	.042	.25	3.42	5.28×10^{-4}	6.20
37	50	2	10	60	1100	100	7.11	5.30	3.46	3.61	2.22	4.46×10^{-6}	5.50×10^{-3}	.0345	.21	3.05	5.93×10^{-4}	5.31
38	50	2	10	60	1100	100	4.80	5.47	2.37	2.49	1.63	6.43×10^{-6}	5.79×10^{-3}	.024	.14	2.35	7.69×10^{-4}	3.84
40	50	2	5	60	1100	200	.841	5.90	.688	.69	.560	1.05×10^{-5}	3.27×10^{-3}	.0275	.08	.645	2.83×10^{-3}	.82
41	50	2	5	60	1100	250	.841	5.74	.649	.62	.532	5.00×10^{-6}	1.47×10^{-3}	.0325	.08	.645	2.83×10^{-3}	.82
42	50	2	5	60	1100	300	.841	5.60	.614	.62	.506	2.80×10^{-6}	7.86×10^{-4}	.037	.07	.645	2.83×10^{-3}	.82
43	50	2	5	60	1100	200	1.63	5.33	1.09	1.09	.847	1.55×10^{-6}	7.26×10^{-4}	.0435	.13	1.09	1.65×10^{-3}	1.51
44	50	2	5	60	1100	200	1.63	5.38	1.11	1.05	.860	1.85×10^{-6}	8.82×10^{-4}	.0445	.13	1.09	1.65×10^{-3}	1.51
45	50	2	5	60	1100	200	.454	6.50	.512	.53	.427	6.77×10^{-6}	1.60×10^{-3}	.0205	.06	.385	4.70×10^{-3}	.46
46	50	2	5	60	1100	250	.452	6.25	.475	.45	.400	2.52×10^{-6}	5.58×10^{-4}	.024	.06	.384	4.72×10^{-3}	.46
47	50	2	5	60	1100	100	2.86	5.28	1.38	1.38	1.03	1.57×10^{-6}	8.95×10^{-4}	.0275	.16	1.65	1.10×10^{-3}	2.92
49	50	2	5	60	1100	150	2.86	4.88	1.35	1.35	1.01	2.59×10^{-7}	1.45×10^{-4}	.0405	.16	1.65	1.10×10^{-3}	2.92

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* Ca denotes total calcium concentration and CO_3 denotes total carbonate concentration.

TABLE 4-3 - EXPERIMENTAL RESULTS - LIMESTONE DISSOLUTION IN DILUTE HCl SOLUTIONS (cont.)

Run No.	Temp. (°C)	Limestone Type	Limestone Wt. (g)	Approx. Mean Particle Size (microns)	Stirrer Speed (RPM)	Feed Flow (ml/min)	HCl Conc. (mmoles/ℓ)	Effluent Concentration (mmole/ℓ) pH	Effluent Concentration (mmole/ℓ) Ca	Effluent Concentration (mmole/ℓ) CO_2	Activity (mmole/ℓ) Ca^{++}	Activity (mmole/ℓ) $CO_3^=$	Relative Saturation $\frac{a_{Ca^{++}} a_{CO_3}}{K_{sp}}$	Dissolution Rate (mmole/g-min	Fraction of Sample Dissolved at 3τ	Equilibrium Activity (mmole/ℓ) Ca^{++}	Equilibrium Activity (mmole/ℓ) $CO_3^=$	Equilibriu Solubility (mmole/ℓ)
50	50	2	7.5	60	1100	150	2.86	5.18	1.38	1.38	1.03	1.01×10^{-8}	5.77×10^{-4}	.028	.11	1.65	1.10×10^{-3}	2.92
51	50	2	10	60	1100	150	2.86	5.43	1.44	1.44	1.07	3.15×10^{-8}	1.86×10^{-3}	.022	.09	1.65	1.10×10^{-3}	2.92
52	50	2	5	60	1100	200	1.58	5.44	.811	**	.645	1.86×10^{-8}	6.63×10^{-4}	.032	.10	1.07	1.69×10^{-3}	1.47
53	50	2	5	60	1100	250	1.58	5.42	.814	**	.647	$1.71.10^{-8}$	6.13×10^{-4}	.041	.10	1.07	1.69×10^{-3}	1.47
54	50	2	5	60	1100	300	1.58	5.35	.793	**	.632	1.23×10^{-8}	4.30×10^{-4}	.048	.10	1.07	1.69×10^{-3}	1.47
55	50	2	3	60	1100	200	1.58	5.00	.774	**	.619	2.55×10^{-7}	8.74×10^{-3}	.052	.15	1.07	1.69×10^{-3}	1.47
56	50	2	4	60	1100	200	1.58	5.38	.811	**	.645	1.43×10^{-8}	5.12×10^{-4}	.041	.12	1.07	1.69×10^{-3}	1.47
57	50	2	7	60	1100	200	1.58	5.60	.838	**	.664	3.78×10^{-8}	1.39×10^{-3}	.024	.07	1.07	1.69×10^{-3}	1.47
65	50	3	4	60	1100	250	1.64	5.40	.855	**	.677	1.65×10^{-8}	6.17×10^{-4}	.053	.13	1.10	1.64×10^{-3}	1.51
66	50	3	4	60	1100	300	1.64	5.02	.831	**	.660	2.99×10^{-7}	1.09×10^{-4}	.062	.12	1.10	1.64×10^{-3}	1.51
67	50	3	4	60	1100	200	1.64	5.20	.812	**	.646	6.52×10^{-7}	2.33×10^{-4}	.041	.12	1.10	1.64×10^{-3}	1.51
68	50	3	4	60	1100	200	1.64	5.50	.858	**	.678	2.54×10^{-8}	9.53×10^{-4}	.043	.13	1.10	1.64×10^{-3}	1.51
72	50	2	5	-325/+400 mesh	1100	300	1.72	4.89	.790	**	.629	1.59×10^{-7}	5.53×10^{-3}	.047	.09	1.14	1.58×10^{-3}	1.58
73	50	2	5	"	1100	200	1.72	5.20	.793	**	.631	6.37×10^{-7}	2.22×10^{-4}	.032	.09	1.14	1.58×10^{-3}	1.58
74	50	2	7	"	1100	200	1.72	5.46	.817	**	.647	2.04×10^{-8}	7.30×10^{-4}	.023	.07	1.14	1.58×10^{-3}	1.58
75	50	2	5	"	1100	250	1.72	4.73	.853	**	.676	8.31×10^{-8}	3.11×10^{-3}	.043	.10	1.14	1.58×10^{-3}	1.58
85	50	2	5	<5	1100	200	1.63	6.3*	1.07*	**	.82	$7.0\ \times10^{-6}$	$3.2\ \times10^{-2}$	.043	.13	1.09	1.65×10^{-3}	1.51
86	50	2	5	<5	1100	300	1.63	6.3*	1.07*	**	.82	$7.0\ \times10^{-6}$	$3.2\ \times10^{-2}$	.064	.13	1.09	1.65×10^{-3}	1.51
87	50	2	3	<5	1100	200	1.63	6.3*	1.07*	**	.82	$7.0\ \times10^{-6}$	$3.2\ \times10^{-2}$	.071	.14	1.09	1.65×10^{-3}	1.51
88	50	2	5	35	1100	300	1.63	5.26	.84	**	.67	8.79×10^{-7}	$3.2\ \times10^{-4}$	.040	.08	1.09	1.65×10^{-3}	1.51
89	50	2	3	35	1100	200	1.63	5.19	.82	**	.65	6.30×10^{-7}	$2.3\ \times10^{-4}$	.043	.13	1.09	1.65×10^{-3}	1.51
90	50	2	5	35	1100	200	1.63	5.50	.88	**	.69	2.60×10^{-8}	$1.0\ \times10^{-3}$	.028	.08	1.09	1.65×10^{-3}	1.51
91	50	2	3	120	1100	200	1.63	4.48	.78	**	.62	2.43×10^{-8}	$8.4\ \times10^{-4}$	.052	.16	1.09	1.65×10^{-3}	1.51
93	50	2	5	120	1100	200	1.63	4.90	.80	**	.64	1.68×10^{-7}	$5.9\times\ 10^{-3}$	.032	.10	1.09	1.65×10^{-3}	1.51
94	50	2	7	120	1100	200	1.63	5.09	.81	**	.645	3.99×10^{-7}	$1.4\times\ 10^{-2}$	.023	.07	1.09	1.65×10^{-3}	1.51

Paper le (DR-004) at the Second International Lime/Limestone Wet Scrubbing Symposium (stone types 2 and 11, respectively, in the referenced paper).

Limestone Weight - The weight of each sample initially charged to the reactor.

Approximate Particle Size - These particle sizes were estimated from photomicrographs of limestone samples. Each size was obtained from a close screen cut so that a narrow distribution was assured.

Stirrer Speed - Stirrer speed was set using a calibrated rheostat. In Runs 14-21, it was later noted that the stirring speed was not reproducible because of friction in the stirrer seal. This problem was solved by using a high-torque stirrer for the remaining runs.

Feed Flow and HCl Concentration - The dilute HCl feed was premixed in the 16-gallon feed tank. The exact concentration was determined by chemical analysis. The feed flow rate through the reactor was measured by a calibrated rotameter.

Effluent Composition - Effluent samples were taken at elapsed times corresponding to 2, 3, 4, and 5 reactor residence times. In Runs 14-51, each sample was analyzed for both total calcium and total carbonate. For experiments using HCl solutions stronger than one mmole/liter, the carbonate concentration was normally within a few percent of the calcium concentration. The carbonate analysis was thus discontinued after Run 51. Analytical results listed in

Table 4-3 are representative steady state values. Analyses for the 3, 4, and 5-residence time samples were typically identical within the accuracy of the techniques used. The effluent pH was measured continuously using a laboratory pH meter with a flow cell arrangement for the electrode.

Ion Activities - The individual ion activities shown in Table 4-3 were calculated using the indicated chemical analyses as input to the previously mentioned chemical equilibrium computer routine. The relative saturation is defined as the ion activity product $a_{Ca^{++}}a_{CO_3^=}$ divided by the solubility product for $CaCO_3$.

Dissolution Rate - Dissolution rates were calculated using the feed flow rate and steady state calcium concentration for each run. The fraction of the initial limestone sample that had dissolved before steady state was approached was also estimated for each run.

Equilibrium Activities and Solubility - These quantities were calculated using the equilibrium computer routine to simulate a saturated solution of limestone in an HCl solution of indicated concentration.

Quantitative interpretation of variable effects such as agitation, temperature, limestone type, and particle size requires a relationship between dissolution rate and liquor composition. When a variable change causes a rate change, a new steady state reactor composition results for a given flow rate and feed composition. This new composition must be considered when comparing dissolution rates among experiments.

Dissolution rates for all dilute HCl experiments using Type 2 limestone at the same levels of temperature, particle size, and agitation are plotted versus hydrogen ion activity in Figure 4-13. For these experiments the variations in liquor composition include concentrations and activities of calcium, carbonate, bicarbonate, hydrogen, and chloride ions.

An attempt was made to correlate results for a single limestone in terms of various measured and calculated parameters describing liquor composition. No generally applicable "driving force" function was found, however. Correlating parameters investigated (in addition to pH) included experimental and equilibrium values for concentrations and activities of calcium, carbonate, and bicarbonate ions.

As may be seen in Figure 4-13, the level of HCl in the reactor feed appears to have some consistent effect on dissolution rates for the same limestone. Least squares lines drawn through data obtained using various acid strengths are shown. At a given pH, the rate of dissolution decreases with chloride concentration for test series at .45, .84, 1.58, and 2.85 mmole Cl/liter. An exception to this trend is noted, however, for Runs 35, 36, 37, and 38 using stronger acid solutions. No explanation for this discrepancy has been found. A duplicate run was conducted to check Run 35 for possible procedural error. Run 117 shown on Figure 4-13 yielded a similar dissolution rate under the same conditions as those used in Run 35.

Experimental and equilibrium activities of dissolving species were calculated for the various runs so that the effect of chloride concentration might be correlated on a more fundamental basis. The difference between equilibrium and actual carbonate ion activities ($a^*_{CO_3^=} - a_{CO_3^=}$) appears to correlate observed dissolution rates quite well, again with the exception of Runs 35-38. Figure 4-14 shows a plot of dissolution rates for

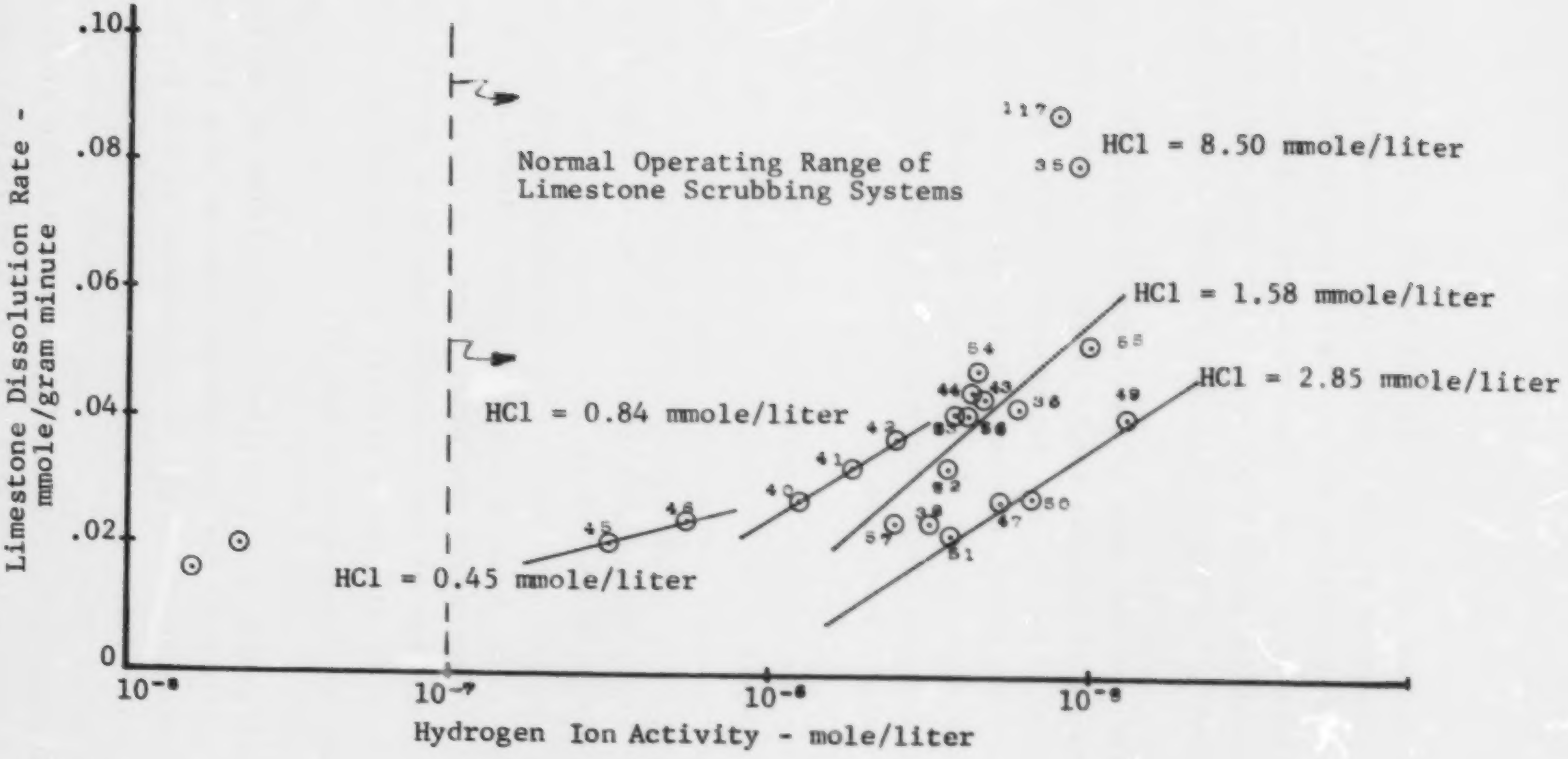

FIGURE 4-13 - LIMESTONE DISSOLUTION RATE VERSUS HYDROGEN ION ACTIVITY - TYPE 2 LIMESTONE IN DILUTE HCl

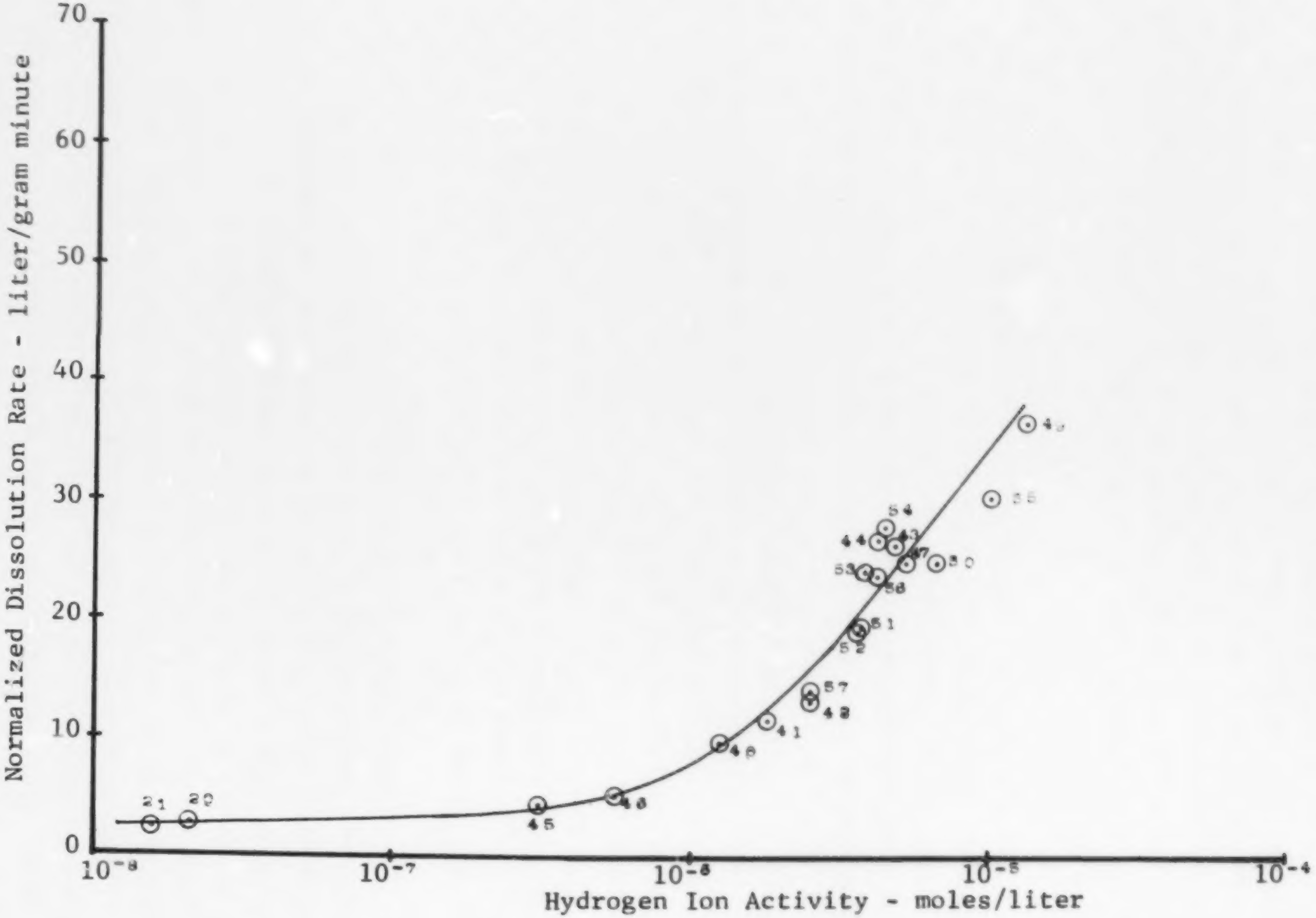

FIGURE 4-14 - NORMALIZED DISSOLUTION RATE $\left[\text{Rate}/\left(a^{*}_{CO_3^=} - a_{CO_3^=}\right)\right]$ VERSUS HYDROGEN ION ACTIVITY - TYPE 2 LIMESTONE IN DILUTE HCl

the Type 2 limestone normalized with respect to the carbonate activity driving force (Rate/($a^{*}_{CO_3^=} - a_{CO_3^=}$). A substantial improvement over Figure 4-13 is seen. Since experiments intended to examine effects of limestone type, agitation, and temperature were conducted within this range of feed liquor concentrations, Figure 4-14 will be used as a basis for interpreting these variable effects.

Experiments using different limestone types are compared to the base case Type 2 limestone dissolution rates in Figure 4-15. Four different limestone types were investigated. Referring to Figure 4-15 experiments using different limestones at similar temperature and agitation include Runs 14, 15, 16, and 17 (Type 1, Austin Limestone), Runs 25, 27, 65, 66, 67, and 68 (Type 3, EPA Hard Calcite), and Runs 29 and 32 (EPA Soft Marl). Significant differences in reactivity between stones are evident in both high and low pH regions. The Type 1 limestone is approximately twice as reactive as the Type 2 (base case) limestone in pH range 6.3 to 6.7. The soft marl appears to be two to three times as reactive as the base case limestone, even under conditions quite close to saturation. The reactivity of the Type 3 limestone is comparable to that of the base case stone over the range of conditions investigated.

Experiments conducted at temperatures other than the usual 50°C temperature include Runs 18, 19, 23, 24, and 30. Dissolution rates for these experiments can be compared with 50°C runs with similar levels of other variables to estimate the temperature dependence of the rate. These runs are shown in Figure 4-16 along with the base case (Type 2) results. Comparing Run 30 to Run 29, for example, a factor of 5.7 difference in dissolution rate (corrected for liquor composition using the carbonate driving force) is seen for a temperature difference of 24°C. This corresponds to an Arrhenius activation energy

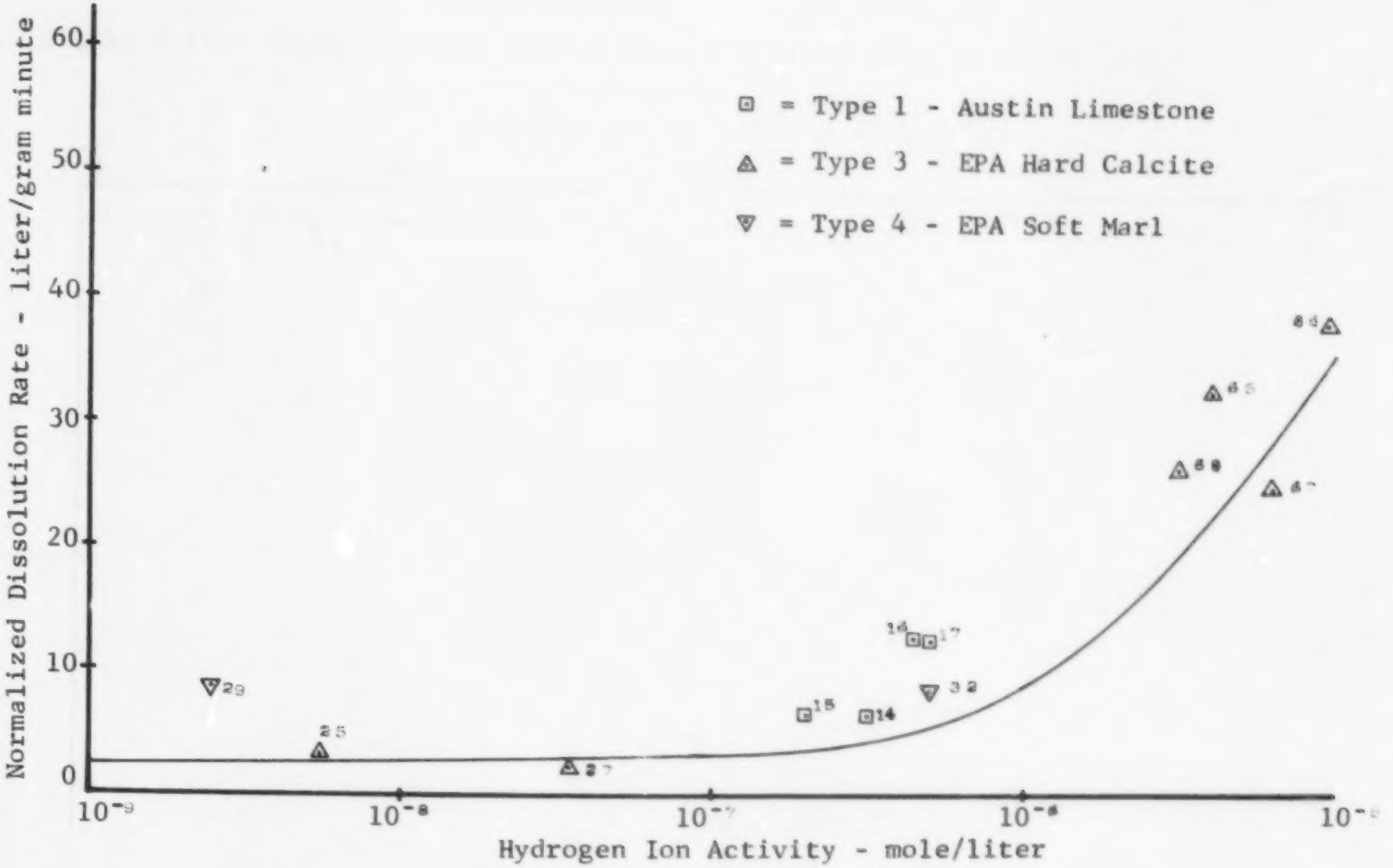

FIGURE 4-15 - EFFECT OF LIMESTONE TYPE ON DISSOLUTION RATE IN DILUTE HCl

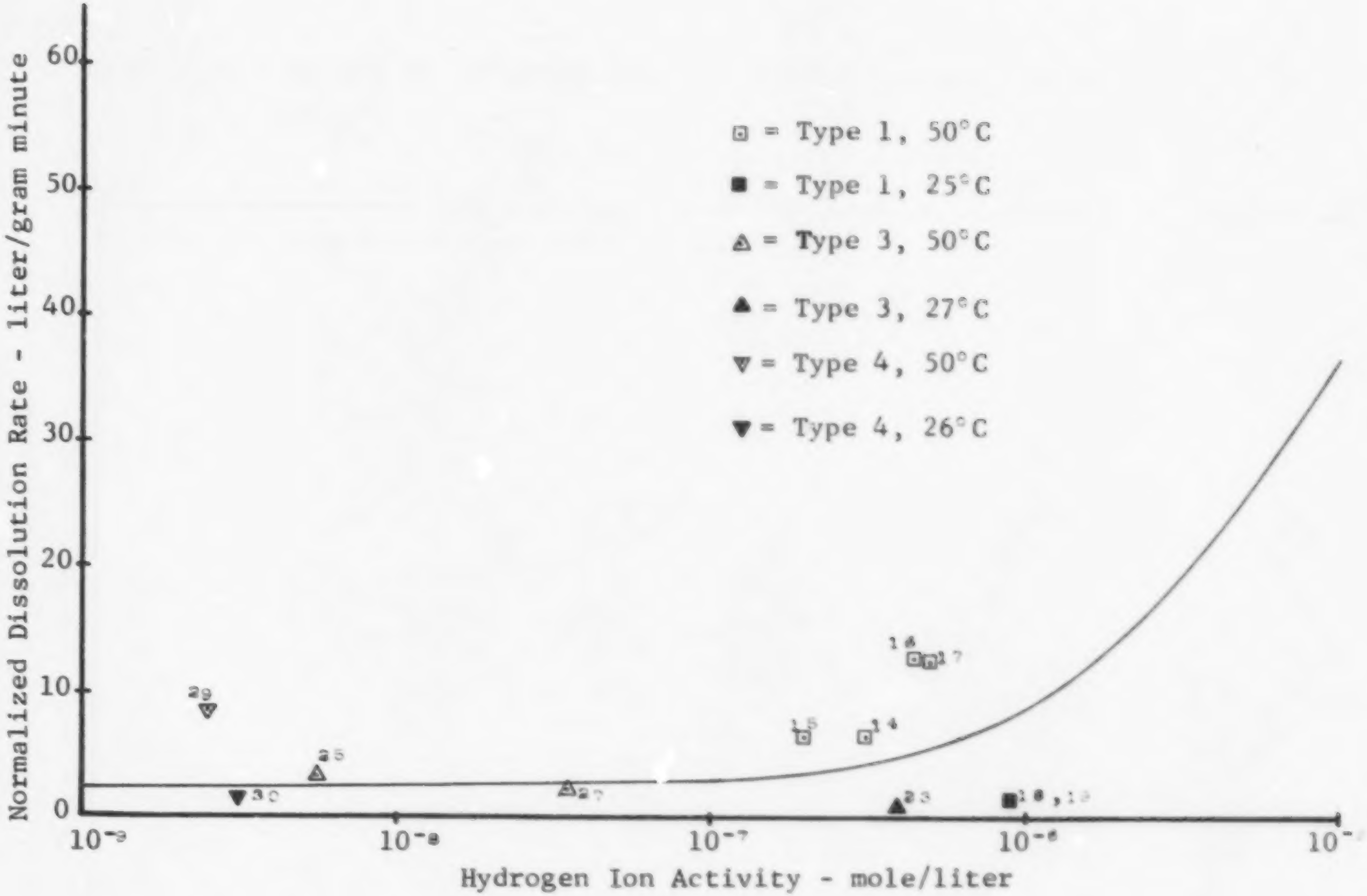

FIGURE 4-16 - EFFECT OF TEMPERATURE ON DISSOLUTION RATE IN DILUTE HCl

of 14 kcal/mole for dissolution of the soft marl in the pH 8.5 range. A factor of six difference in rate is observed for the hard calcite at a pH of 6.4. This also leads to an activation energy of 14 kcal/mole. A third comparison using Runs 18 and 19 with Austin limestone shows a similar temperature dependence.

The effect of stirring rate may be seen by comparing Runs 23 and 24 using calcite at 27°C, Runs 27 and 28 with calcite at 50°C, and Runs 32 and 33 using marl at 50°C. These results are shown in Figure 4-17. In each of these cases, a significant effect of stirring is seen. A quantitative estimate of this effect would require more difinitive data describing the rate dependence on liquor composition. The observed stirring effect is significant both at high and low temperatures and pH levels.

Experiments intended to investigate the effect of particle size on dissolution rate were conducted using the Type 2 limestone. Dissolution rates of 120 micron and ~ 5 micron limestone samples are compared to those of the base case (60 micron) limestone in Figure 4-18. The dissolution rate of 60 micron limestone particles is approximately twice that of 120 micron particles. A sample having a mean size of approximately 5 microns dissolved 5 to 8 times faster than the 60 micron material.

The scatter in the small particle size data shown in Figure 4-18 is due to the broad size distribution of these samples. All samples larger than a 400 mesh screen could be classified into reasonably narrow size cuts. The fines used in Runs 85, 86, and 87 had a wider range of particle sizes, however. With the batch dissolution technique used in this study, a steady state composition is not achieved under these circumstances. The indicated pH of 6.3 for these three tests is a representative estimate. Actual operating pH typically ranged from 5.8 to 6.7 over the course of a run.

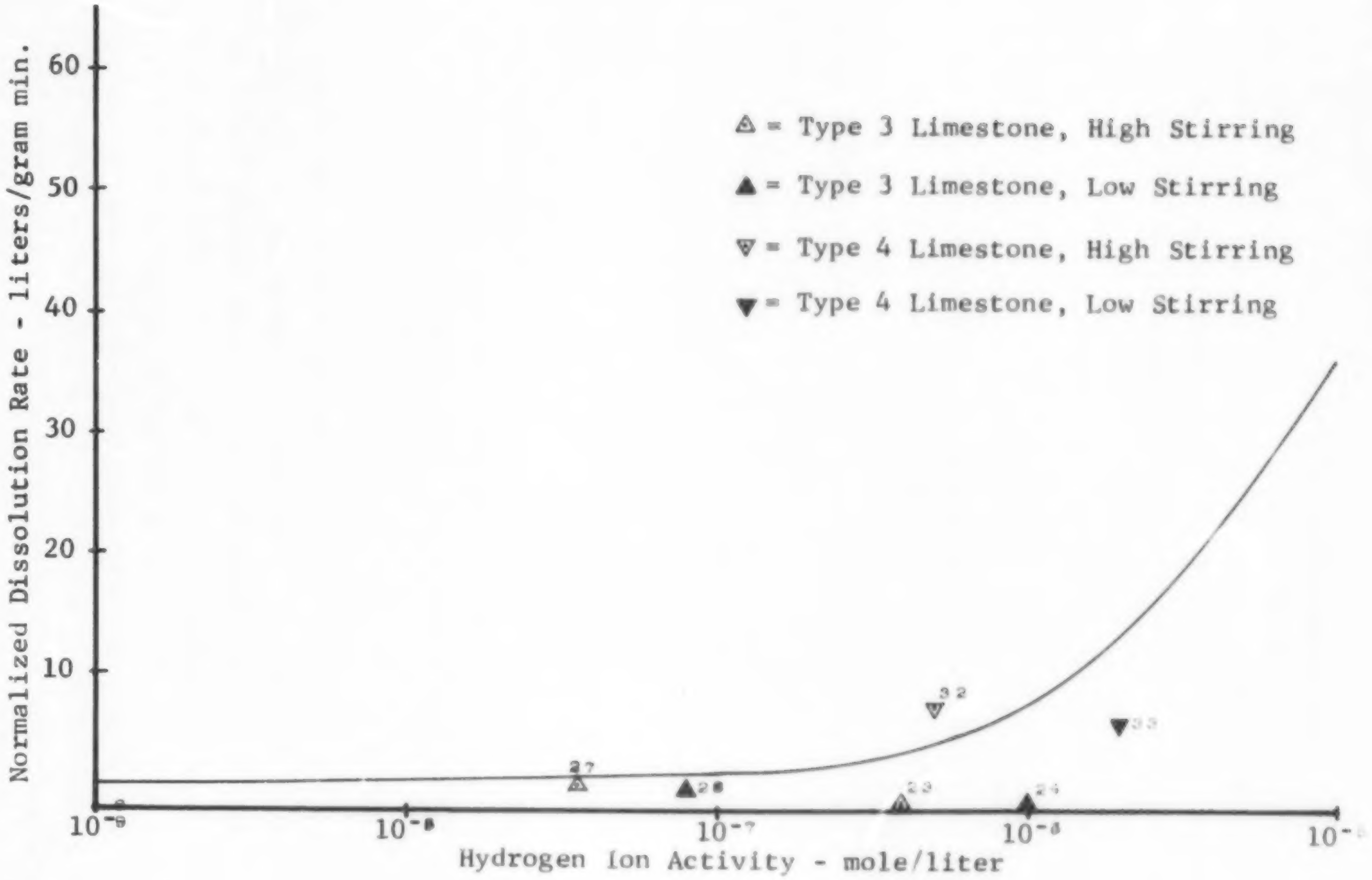

FIGURE 4-17 - EFFECT OF STIRRING ON DISSOLUTION RATE IN DILUTE HCl

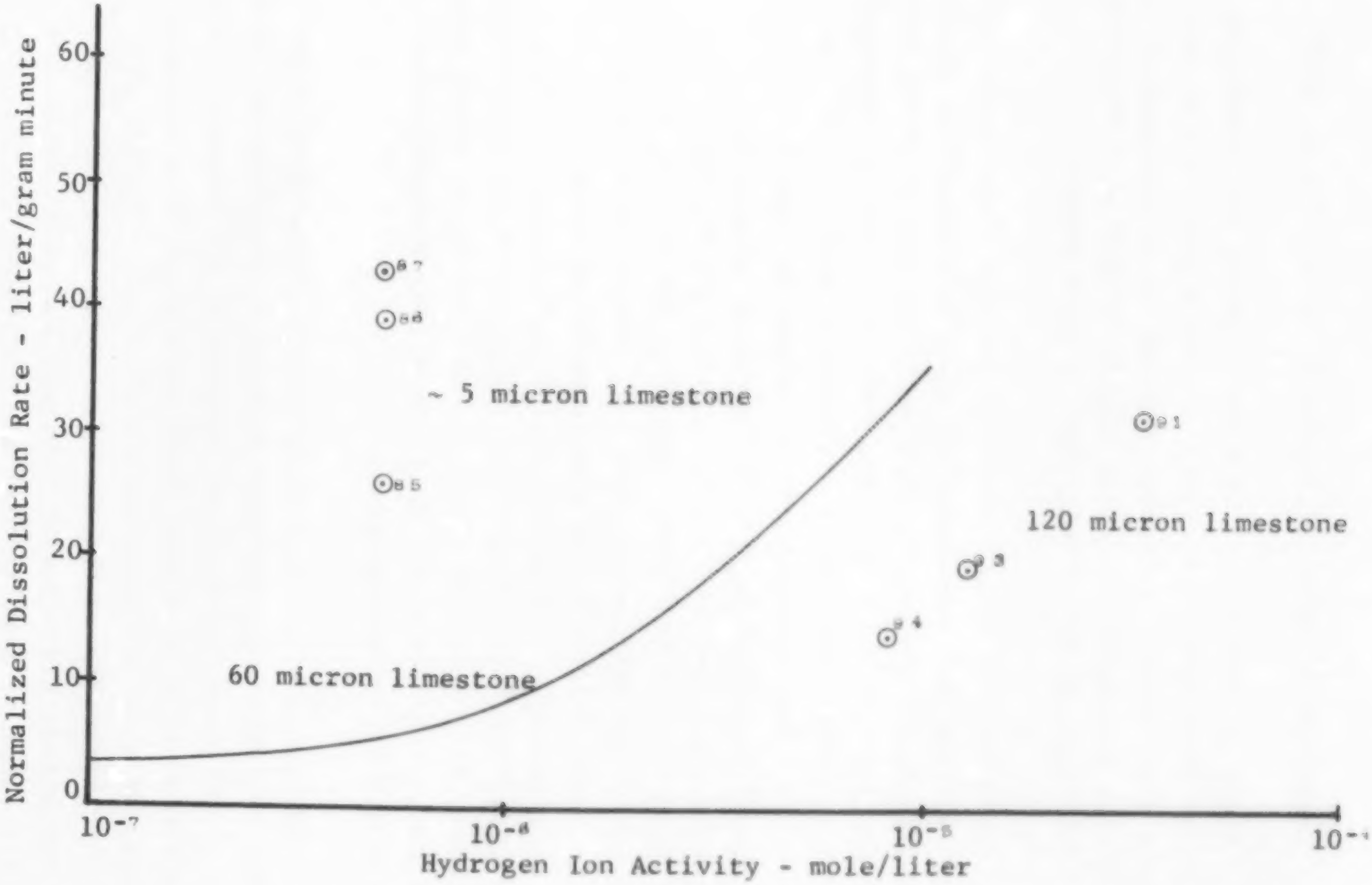

FIGURE 4-18 - EFFECT OF PARTICLE SIZE ON DISSOLUTION RATE - TYPE 2 LIMESTONE IN DILUTE HCl

4.4.2 Limestone Dissolution in Simulated Scrubbing Liquor

Since no fundamental rate correlation was developed for limestone dissolution in dilute HCl solutions, additional experiments were run using liquors typical of those encountered in closed-loop limestone scrubbing units. These data should be more directly applicable to full scale system design.

Selection of liquor compositions for these tests was based both on computer simulation of limestone scrubbing systems and actual analyses of samples from operating pilot units. This information has shown that the concentrations of important species in solution vary substantially only according to the characteristic ionic strength of the particular system. A typical limestone scrubbing liquor is essentially a slightly supersaturated solution of calcium sulfite and sulfate. The solubilities of these compounds determine the amounts of calcium, sulfite, and sulfate in solution. Their solubilities are in turn influenced strongly by the presence of other "soluble" species, particularly sodium, magnesium, and chloride. Concentrations of soluble species are determined by trace constituents in limestone, flue gas, and fly ash. The degree to which solid waste is dewatered also has a major impact on concentration levels reached by soluble species.

Two types of simulated scrubbing liquor were used. These were estimated to represent a range of compositions which might be experienced in field application of the process. Runs 95-98 were conducted in a high ionic strength liquor containing high levels of soluble magnesium and chloride. Sulfite and sulfate concentrations in the feed for these runs were estimated so that the steady state reactor composition would be in the appropriate range of supersaturations for these species.

Steady state levels of calcium concentration for this series ranged from 36.9 to 39.7 millimole/liter. Calcium sulfite supersaturations were in the 4-5 range and sulfate supersaturations ranged from 1.0 to 1.05. These are typical of hold tank operating conditions measured at several pilot units.

Runs 107-110 used a feed liquor with no soluble magnesium and only small amounts of sodium and chloride. Operating concentrations of calcium were much lower in this case; about 22 millimole/liter. Calcium sulfite and sulfate supersaturations were about 2 and 1.3, respectively.

A third series of experiments, Runs 111-115, was carried out using a similar low ionic strength feed liquor with a slightly higher HCl concentration. The operating combination of a stronger acid feed at a lower flow rate using large limestone samples yields a larger change in calcium concentration from feed to effluent and, thus, a more accurate dissolution rate calculation.

Complete operating conditions and analytical results for the simulated scrubbing liquor test series are summarized in Table 4-4. Dissolution rates observed in these simulated scrubber liquors are not related to the dilute HCl experimental results by the carbonate ion activity expression discussed in Section 4.4.1. No satisfactory expression has been found to quantitatively account for increased dissolution rates in simulated scrubbing liquor.

Figure 4-19 shows dissolution rates for the Type 2 limestone in simulated scrubbing liquor experiments. A least squares fit of data from dilute HCl runs in the same pH range is also shown for comparison. The rates in scrubber liquor are

TABLE 6-6

LIMESTONE DISSOLUTION IN SIMULATED SCRUBBER LIQUOR

Run No.	Temp. °C	Limestone		Approx. Mean Particle Size (Micron)	Stirrer Speed (RPM)	Feed Flow Rate (ml/min)	Feed Composition (mmole/liter)						Effluent Concentration (mmole/ℓ)			Activity (mmole/ℓ)		Relative Saturation $\frac{a_{Ca^{++}} a_{CO_3^=}}{K_{sp}}$	Dissolution Rate (mmole/gram-min)	Fraction of Sample Dissolved at 3τ	Equilibrium Activity (mmole/ℓ)		Equilib. Solubil. (mmole/ℓ)
		Type	Wt. (g)				Ca	Mg	Na	Cl	SO_3	SO_4	pH	Ca	CO_2	Ca^{++}	$CO_3^=$				Ca^{++}	$CO_3^=$	
95	50	2	5	60	1100	200	36.3	168	18.7	322	11.6	70.4	5.40	39.1	2.1	7.36	3.78×10^{-6}	1.5×10^{-2}	.11	.33	7.8	2.3×10^{-4}	6.8
96	50	2	5	60	1100	300	36.4	168	18.7	322	11.6	70.4	5.30	39.7	2.0	7.51	2.40×10^{-6}	1.0×10^{-2}	.20	.40	7.8	2.3×10^{-4}	6.8
97	50	2	3	60	1100	200	34.3	168	18.7	322	11.6	70.4	5.25	36.9	1.3	7.01	1.19×10^{-5}	4.6×10^{-2}	.17	.51	7.8	2.3×10^{-4}	6.8
98	50	2	7	60	1100	200	34.3	168	18.7	322	10.8	70.4	5.60	37.6	2.2	7.01	8.69×10^{-6}	3.4×10^{-2}	.096	.28	7.8	2.3×10^{-4}	6.8
107	50	2	5	60	1100	200	19.6	—	13.2	6.60	3.53	22.4	5.53	22.7		5.76	4.84×10^{-6}	1.5×10^{-2}	.133	.40	5.3	3.3×10^{-4}	3.6
108	50	2	5	60	1100	300	19.6	—	13.2	6.60	3.67	22.3	5.33	22.2	1.54	5.66	2.14×10^{-5}	6.7×10^{-2}	.168	.36	5.3	3.3×10^{-4}	3.6
109	50	2	3	60	1100	200	19.6	—	13.2	6.60	3.37	22.6	5.04	22.0	1.37	5.63	5.36×10^{-7}	1.7×10^{-3}	.173	.52	5.3	3.3×10^{-4}	3.6
110	50	2	7	60	1100	200	19.4	—	13.2	6.60	3.08	22.8	5.59	21.4	1.62	5.33	6.7×10^{-6}	2.0×10^{-2}	.057	.17	5.3	3.3×10^{-4}	3.6
111	50	2	20	60	1100	50	16.7	—	10.0	15.35	—	19.9	5.70	23.0	9.26	6.20	5.9×10^{-7}	2.0×10^{-3}	.016	.19	6.69	2.70×10^{-4}	8.4
112	50	2	30	60	1100	50	15.7	—	10.0	15.35	—	19.9	5.80	22.7	9.26	6.08	9.3×10^{-7}	3.1×10^{-3}	.012	.16	6.69	2.70×10^{-4}	9.4
113	50	2	20	60	1100	50	17.6	—	10.0	15.35	—	19.9	5.77	33.1	6.93	6.24	3.9×10^{-7}	2.0×10^{-3}	.016	.17	6.63	2.73×10^{-4}	7.1
114	50	2	30	60	1100	50	19.35	—	10.0	15.35	—	19.9	6.00	22.6	4.95	6.10	9.9×10^{-7}	3.4×10^{-3}	.0054	.08	6.63	2.73×10^{-4}	5.6
115	50	2	30	60	1100	50	20.5	—	10.0	15.7	—	19.6	6.16	22.9	3.76	6.23	1.3×10^{-6}	4.6×10^{-3}	.006	.05	6.40	2.84×10^{-4}	3.0

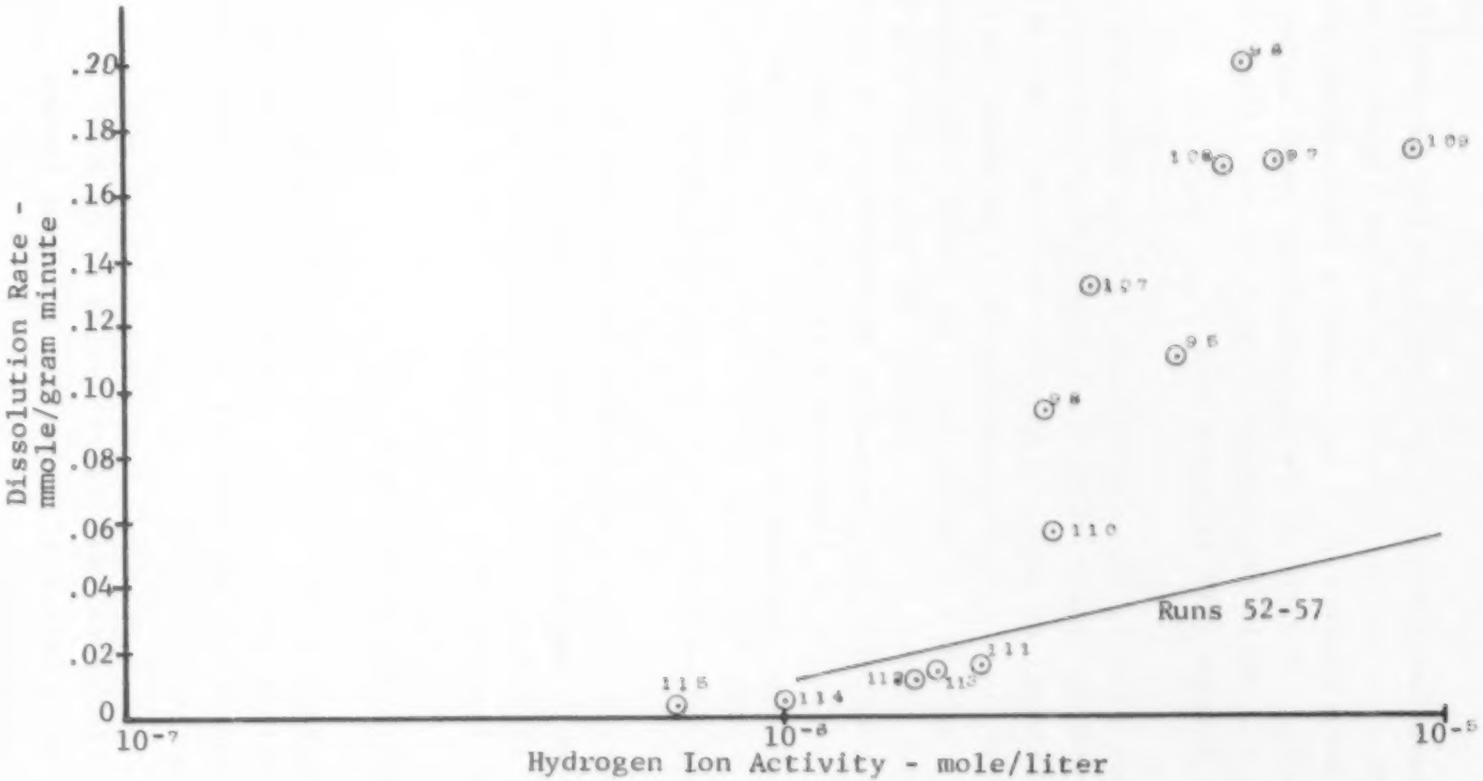

FIGURE 4-19 - LIMESTONE DISSOLUTION IN SIMULATED SCRUBBER LIQUOR

lower than those for the dilute HCl solution for pH levels above about 5.7. This is not unreasonable since the liquor in which Runs 111-118 were conducted is very close to saturation with respect to $CaCO_3$. The pH of the saturated scrubber liquor is approximately 6.2 while the equilibrium pH of the dilute HCl runs shown in Figure 4-19 is about 7.3.

Below pH 5.7, the dissolution rate of limestone in simulated scrubbing liquor exhibits a substantial increase, roughly proportional to the hydrogen ion activity. The dissolution rate at pH 5 is approximately 30 to 40 times that at pH 6. This behavior compares very well with dissolution rate behavior observed in pilot units. For example, in the pilot studies conducted at Combustion Engineering's Windsor laboratory, the amount of limestone dissolution in the scrubber at pH 5 was comparable to that in the hold tank at pH 6 even though the volume of liquor in the scrubber was a factor of 20 less than that in the hold tank.

Figure 4-19 also shows that the presence of large amounts of soluble magnesium and chloride does not appear to have a significant effect on dissolution in simulated scrubber liquor. Runs 95-98 resulted in rates comparable to Runs 108-110.

4.4.3 Summary and Conclusions

Limestone dissolution rate experiments have been conducted in dilute HCl solutions and simulated scrubbing liquors. In the dilute HCl test series, the following variable effects were noted.

> Limestone reactivity varied by as much as a factor of three for the four stones investigated.

- The temperature dependence of the dissolution rate corresponds to an Arrhenius activation energy of about 14,000 calories/gram-mole.

- A significant agitation effect was seen at high and low levels of temperature and pH.

- The dissolution rate is approximately inversely proportional to particle size. The dissolution rate per unit of surface area is thus nearly constant.

These experimental observations indicate that limestone dissolution is probably limited by both surface phenomena and liquid film resistance. General correlation of results in this case would be particularly difficult.

Limestone dissolution rates in simulated scrubbing liquor could not be related to the dilute HCl test results in any consistent fashion. Experimental results for these tests showed that dissolution rates can be expected to be a strong function of pH. Soluble magnesium and chloride, on the other hand, do not appear to affect the dissolution rate in simulated scrubber liquor.

For purposes of process design estimates, the following may be used.

- Limestone dissolution rates in a hold tank environment (pH 6) should be on the order of 1×10^{-5} moles per minute per gram of limestone for 60 micron particles. The rate on a per gram of stone basis is inversely proportional to particle size.

- Limestone dissolution rates in a scrubber environment (pH 5) should be 30 to 40 times the hold tank rate. Thus significant limestone dissolution will occur in most scrubbers in spite of the low liquid hold up compared to that of a hold tank.

In view of the demonstrated complexity of limestone dissolution rate correlation, laboratory evaluation of candidate limestones is recommended as a standard design procedure. These tests should be conducted using a liquor typical of design operating conditions for the hold tank and scrubber environments.

4.5 Lime Dissolution

The experimental apparatus and technique discussed in previous sections did not prove suitable for measurement of lime dissolution kinetics. Instead, other methods were used to demonstrate qualitatively the high dissolution rate of commercially available hydrated lime.

4.5.1 Simplified Beaker Experiments

Initial experimental work was directed toward determining rough order-of-magnitude values for the dissolution rates of lime in aqueous solutions. Samples of the lime used by Southern California Edison in their pilot SO_2 scrubber at Mohave were obtained for these experiments.

A microscopic examination of this material showed that it was composed mainly of 1-2 micron diameter particles. A chemical analysis of a sample of this lime yielded the results shown below:

Sample: Hydrated Lime
Source: Southern California Edison Company, Mohave Generating Station (Manufactured by Flintkote)

Component	Wt.%
Na	0.8
Mg	0.25
Ca	48.2

During these initial experiments, one gram samples of this material were dropped into a stirred beaker containing either deionized water or dilute hydrochloric acid solutions. The dissolution of the lime was monitored with a divalent cation electrode which measured the activity of the Ca^{++} (or other divalent) ions in the solution.

Based on the output of this electrode observed during these experiments, it was obvious that the Ca^{++} ion activity approached its equilibrium value very rapidly. For all of the cases considered, greater than 90% approach of the measured activity to its equilibrium value was achieved 15-20 seconds after the lime sample was added to the beaker. Limestone samples tested in this manner dissolved considerably slower, however it was not known how much of this observed rate difference was due to the smaller size of the lime particles involved. (1-2 micron for lime vs. ≈50 micron for limestone).

In order to minimize the rate effects caused by particle size differences between samples of commercial lime and limestone, these tests were repeated using reagent samples of $CaCO_3$ (limestone), CaO (quicklime), and $Ca(OH)_2$ (hydrated lime). Microscopic examination of these reagents showed that all three samples were composed of particles which were approximately 1 micron in diameter.

Samples of 0.1 grams each of these reagents were added to a well-stirred one liter beaker. Dissolution rates were monitored with a pH electrode. This electrode was used in these experiments because its response characteristics were better than those obtained with the divalent ion electrode.

The response time of the pH electrode and the mixing time of the agitated vessel were determined by dumping small samples of concentrated HCl or NaOH solutions into the vessel. A typical response curve for this type of experiment is shown in Figure 4-20. It can be seen from this curve that the pH electrode output reached its new steady state value about two seconds after the alkaline liquid was added to the reactor. This response time was lower for less drastic changes in pH. The divalent ion electrode took about five seconds to respond to the addition of a saturated lime solution.

Prior to the start of each dissolution experiment the reactor was filled with deionized water and the initial pH was adjusted using dilute solutions of HCl and NaOH. Experiments were conducted using each of the three reagents at initial pH values of 5 and 7. Typical pH electrode response curves for these experiments are shown in Figures 4-21 and 4-22.

No significant differences in dissolution rate could be observed between the CaO and $Ca(OH)_2$ reagent samples at either pH. As can be seen from Figures 4-21 and 4-22, however $CaCO_3$ was observed to dissolve much slower than either CaO or $Ca(OH)_2$.

Based upon these results, it was concluded that commercial lime samples can be expected to dissolve considerably faster than limestone. This observed rate difference is due to a combination of the following two factors.

- the intrinsic dissolution rate of lime is greater than that of limestone, and

- commercial lime particles are usually much smaller in size than limestone particles.

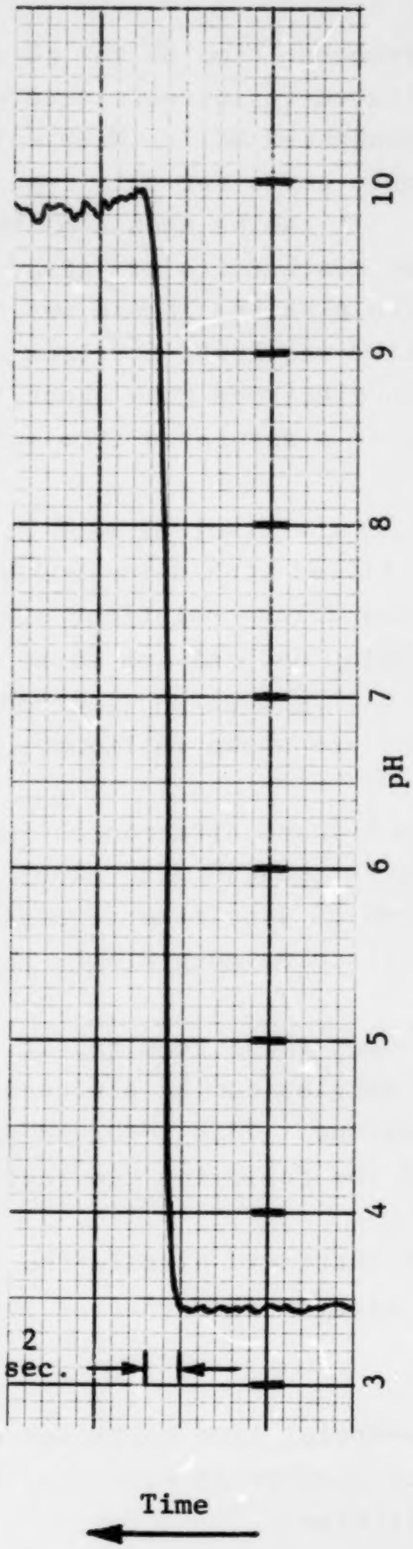

FIGURE 4-20 - pH ELECTRODE RESPONSE

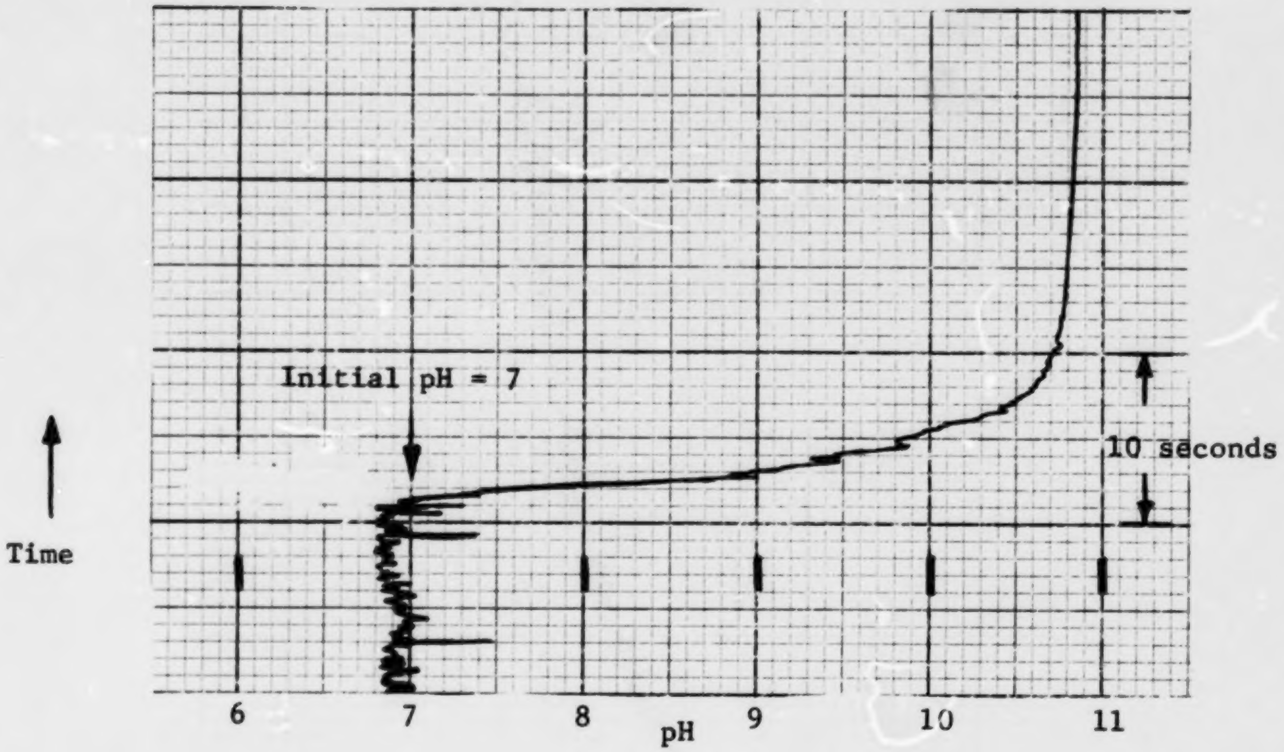

FIGURE 4-21 - DISSOLUTION OF $Ca(OH)_2$ REAGENT IN DEIONIZED WATER

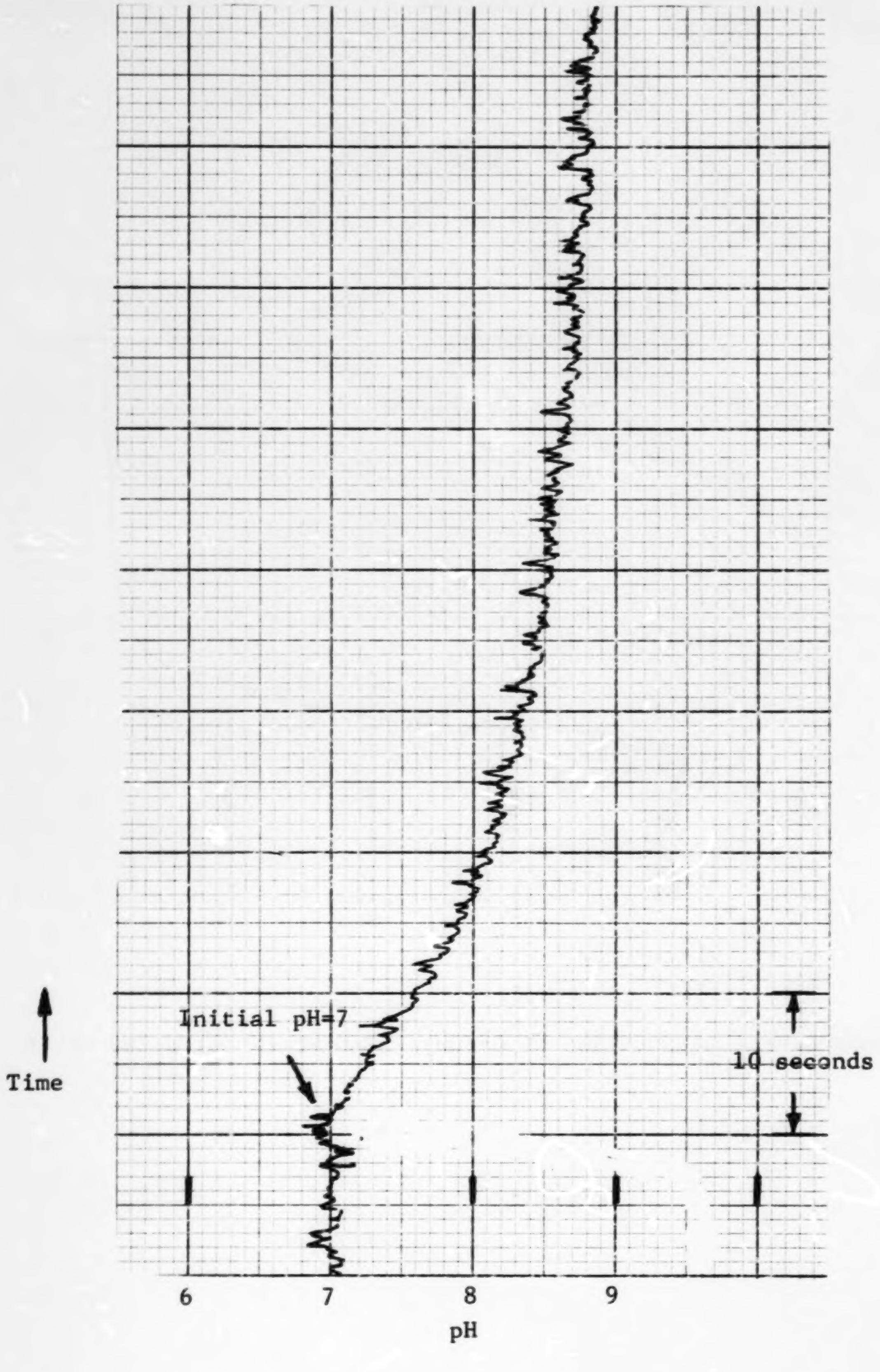

FIGURE 4-22 - DISSOLUTION OF $CaCO_3$ REAGENT IN DEIONIZED WATER

The process implications of these findings can be summarized as follows. Because of the high dissolution rate of lime, a circulating lime slurry leaving an SO_2 scrubber hold tank or other long residence time vessel will be essentially saturated with respect to $Ca(OH)_2$ in the liquid phase. This will not necessarily be the case in a low residence time vessel such as a spray scrubber.

4.5.2 Packed Bed Reactor Experiments

In an attempt to quantitatively describe the dissolution rate of lime in aqueous solutions, a low-residence-time plug flow reactor was constructed. In this reactor the liquid phase was forced down through a fixed bed of lime particles. The residence time of the liquid in the packed bed was controlled by adjusting the flow of liquid to the reactor.

Unfortunately, this reactor design proved to be unsuitable because of the small sizes of the lime particles used. Apparently, these particles plugged the pores of the Millipore filter which supported the bed. This resulted in the buildup of a large pressure drop across the reactor and severely limited the amount of liquid which could be forced through the reactor.

In an effort to circumvent this problem, several attempts were made at growing larger lime particles. This was done by adding a dilute aqueous solution of $CaCl_2$ dropwise to a solution of NaOH. A small number of lime crystals greater than 10 micron in diameter were successfully grown using this technique; however, the yield of large crystals was so poor that this approach had to be abandoned.

4.5.3 Spray Tower Experiments

As noted previously, there is no real incentive from a process standpoint for investigating the rate of lime dissolution in a typical stirred process hold tank. When lime particles are present in any agitated, long residence time vessel, the liquid phase will become essentially saturated with respect to $Ca(OH)_2$. In a short residence time vessel (i.e., a scrubber), however, a consideration of the kinetics of lime dissolution might be of interest. This is particularly true if the lime dissolves so fast that a significant portion of the effective alkalinity in the scrubber can be contributed by lime species which enter the scrubber initially in the solid phase. If this is the case the concentration of lime solids in the inlet liquor must be considered as an important scrubber design variable.

In order to investigate this phenomenon, a series of SO_2 sorption experiments was conducted using Radian's bench-scale scrubbing apparatus. These experiments were designed to determine whether or not a significant quantity of lime can dissolve in a typical short residence time contactor.

A schematic diagram of the experimental apparatus used for this study is shown in Figure 4-23. This equipment was designed to supply a three-inch diameter glass scrubber with known quantities of a blended gas mixture which simulated a typical power plant flue gas. Inside the scrubber the gas mixture was countercurrently contacted with the liquid sorbent. In all of the SO_2 sorption experiments reported here, the scrubber was equipped with a single spray nozzle as shown in Figure 4-24.

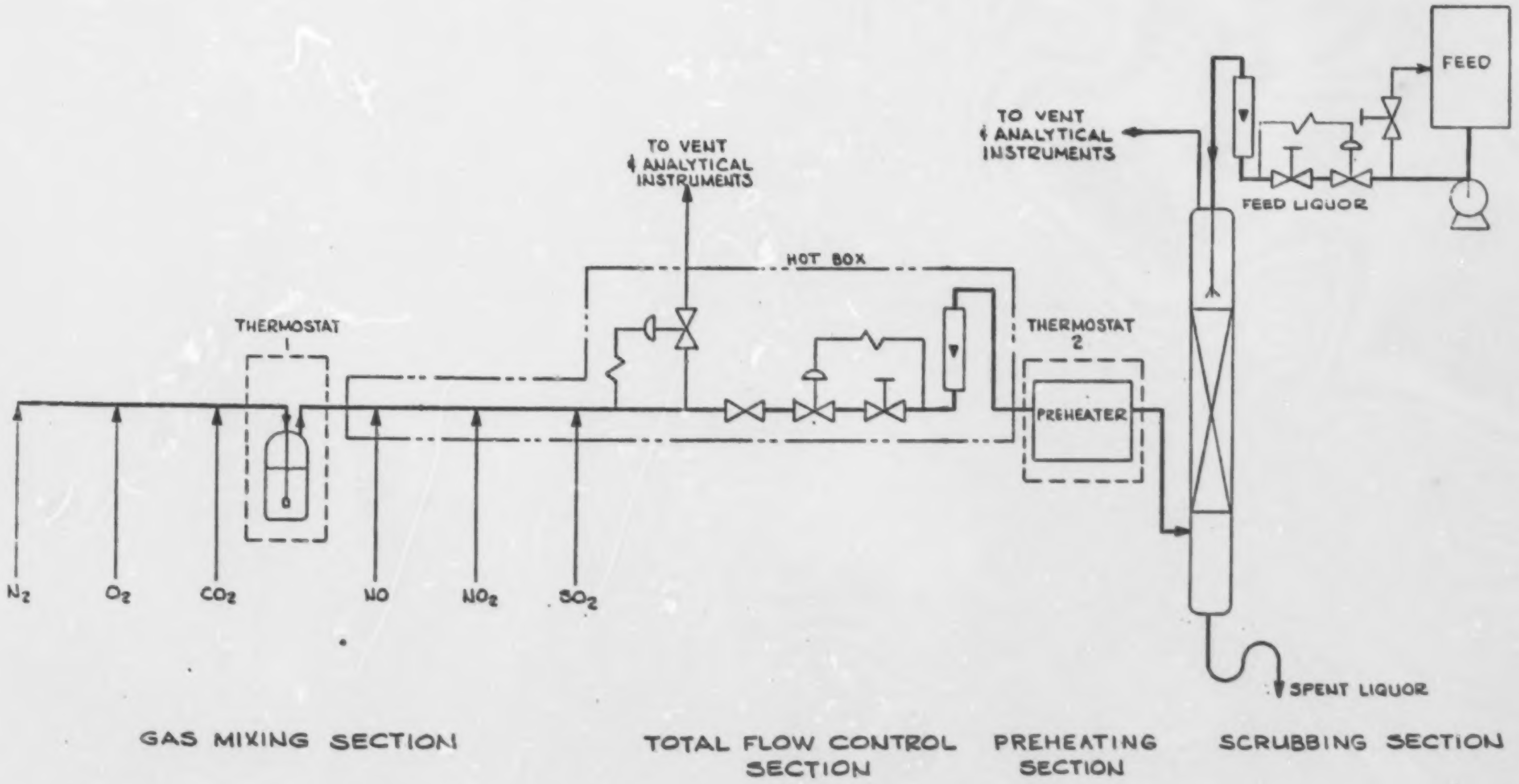
TO VENT
& ANALYTICAL
INSTRUMENTS
TO VENT
& ANALYTICAL
INSTRUMENTS
FEED
FEED LIQUOR
HOT BOX
THERMOSTAT
1
THERMOSTAT
2
PREHEATER
SPENT LIQUOR
N_2
O_2
CO_2
NO
NO_2
SO_2
GAS MIXING SECTION
TOTAL FLOW CONTROL SECTION
PREHEATING SECTION
SCRUBBING SECTION

FIGURE 4-23 - EXPERIMENTAL APPARATUS

Radian
82-1
5/11/72

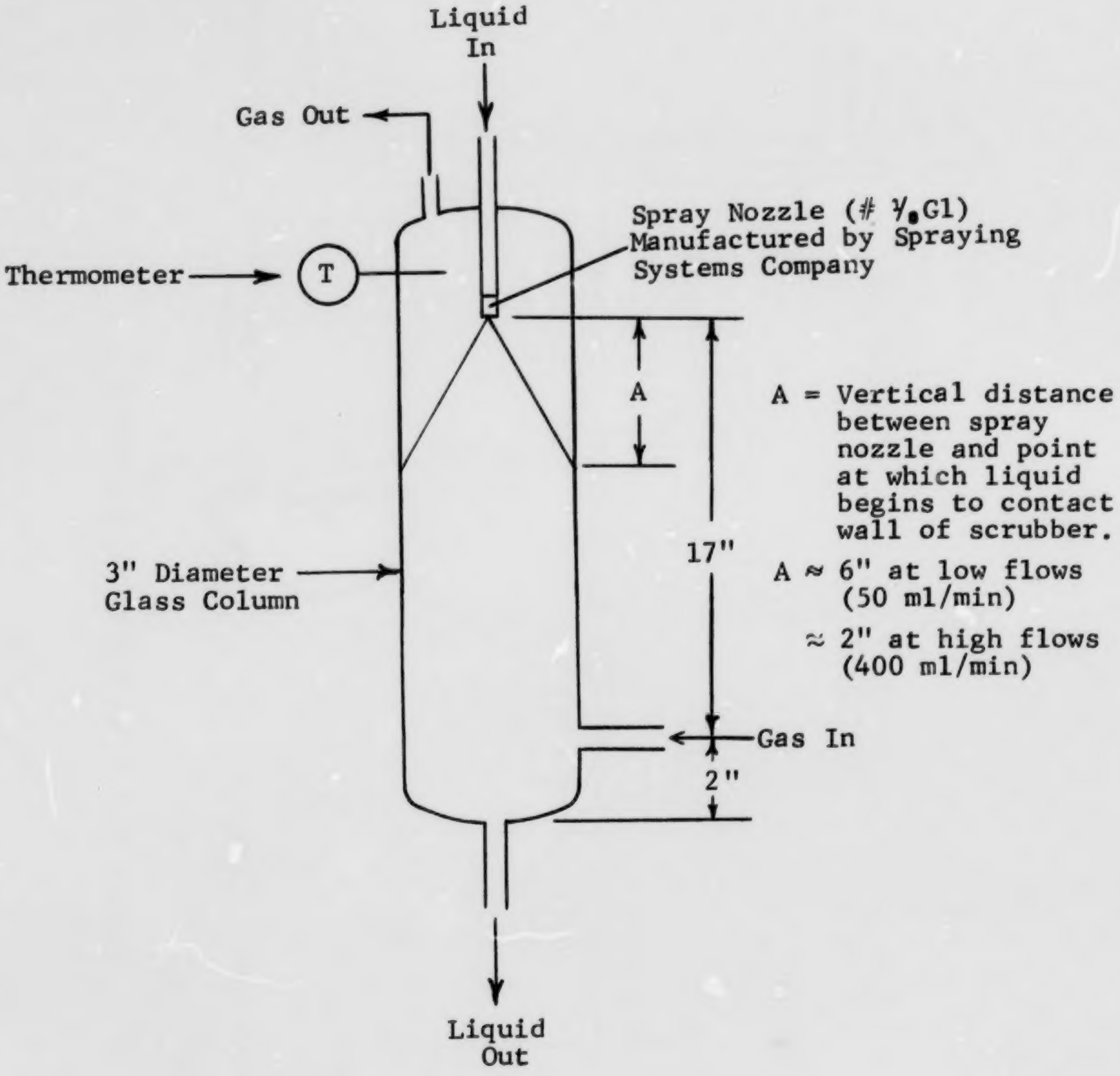
Liquid In
Gas Out
Spray Nozzle (# 1/8G1) Manufactured by Spraying Systems Company
Thermometer
T
A
A = Vertical distance between spray nozzle and point at which liquid begins to contact wall of scrubber.
A ≈ 6" at low flows (50 ml/min)
≈ 2" at high flows (400 ml/min)
17"
3" Diameter Glass Column
Gas In
2"
Liquid Out

FIGURE 4-24 - DIAGRAM OF SPRAY SCRUBBER USED IN LIME DISSOLUTION RATE STUDY

Sampling connections were provided on all streams entering and leaving the scrubber. The capability for obtaining on-line vapor phase SO_2 analyses was supplied by a DuPont Model 400 photometric analyzer. Gas and liquid phase flow rates were determined by using calibrated rotameters.

The rate of lime dissolution could not be determined by conventional slurry sampling techniques since the residence time of a pump/filter combination would be perhaps five to ten times that of the spray tower. Instead, interpretation of these experiments had to be based on the degree of SO_2 removal obtained in the scrubber.

First, the efficiency of the spray tower was determined using NaOH solutions at various liquid rates. These runs employed very high pH liquors to minimize the liquid film resistance to mass transfer. This provided a means of estimating the amount of interfacial mass transfer surface area generated in the scrubber as a function of the mass flow of liquid through the spray nozzle. This information was needed to normalize the results obtained from sorption experiments which were conducted using lime slurries of varying solids content.

Liquid rates which were used during the lime slurry experiments were chosen in such a way that different scrubbing liquors were compared under conditions at which the total alkalinity (liquid + solid) fed to the spray tower was constant. The effect upon the SO_2 removal of having the alkalinity in the solid rather than the liquid phase was then considered, once a correction was made for liquid rate effects.

The raw data obtained during the lime scrubbing experiments are presented in Table 4-5. Shown in this table are data from runs which were made using a 0.5 M NaOH scrubbing solution (Runs 1-6), a saturated lime solution (Runs 7-15), and lime slurries containing from 0.1 to 0.5 wt.% $Ca(OH)_2$ solids (Runs 16-60).

The calculated stoichiometric ratios shown in this table were determined by assuming that the following SO_2 sorption reactions take place.

Reaction with NaOH:

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O \qquad (4\text{-}11)$$

Reaction with Lime:

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O \qquad (4\text{-}12)$$

A calculated stoichiometric ratio of 1.0 is obtained when the molar flow rate of NaOH [or $Ca(OH)_2$] is exactly equal to the amount required to react with 100% of the inlet vapor phase SO_2 according to the reaction given in Equation 4-11 (or 4-12).

A detailed analysis of the experimental results presented in Table 4-5 is presented in the following section.

TABLE 4-5

BENCH-SCALE SPRAY COLUMN SO$_2$ SORPTION RESULTS

(Temperature: 50°C)

Run No.	Gas Flow SCFH*	SO$_2$ Concentration Inlet	SO$_2$ Concentration Outlet	Scrubbing Liquid	Liquid Flow ml/min	Mol.% SO$_2$ Scrubbed	Stoichiometry (based on inlet SO$_2$)	No. of Transfer Units (assuming zero SO$_2$ back pressure)
1	95	2950	1550	.5 M NaOH	80	47.5	3.32	0.64
2	95	3000	910	"	112	69.7	4.66	1.19
3	95	3000	630	"	157	79.0	6.53	1.56
4	95	3000	395	"	240	86.8	9.98	2.03
5	95	3000	240	"	300	92.0	12.48	2.53
6	95	3000	100	"	400	96.7	16.64	3.40
7	95	3000	2325	.016 M Ca(OH)$_2$ (saturated)	93	22.5	0.24	0.25
8	95	3000	1975	"	135	34.2	0.36	0.42
9	95	3000	1765	"	180	41.2	0.48	0.53
10	95	3000	1175	"	220	60.8	0.58	0.96
11	95	3000	975	"	263	67.5	0.70	1.12
12	95	3000	750	"	305	75.0	0.81	1.39
13	95	3000	575	"	345	80.8	0.92	1.65
14	95	3000	450	"	388	85.0	1.03	1.90
15	95	3000	325	"	428	89.2	1.14	2.22
16	95	3000	2675	.1 Wt.% Ca(OH)$_2$ Slurry	60	10.8	0.30	0.11
17	95	3000	2125	"	89	29.2	0.44	0.34
18	95	3000	1775	"	138	40.8	0.69	0.52
19	95	3000	1175	"	172	60.8	0.86	0.94
20	95	3000	725	"	225	75.8	1.13	1.42
21	95	3000	425	"	310	85.8	1.55	1.95
22	95	3000	300	"	350	90.0	1.75	2.30
23	95	3000	250	"	393	91.7	1.97	2.48
24	95	3000	175	"	435	94.2	2.18	2.84
25	95	3000	1050	.2 Wt.% Ca(OH)$_2$ Slurry	31	65.0	0.22	1.05
26	95	3000	775	"	75	74.2	0.54	1.35
27	95	3000	550	"	119	81.7	0.86	1.70
28	95	3000	350	"	161	88.3	1.17	2.15
29	95	3000	175	"	228	94.2	1.65	2.84
30	95	3000	140	"	267	95.3	1.94	3.06
31	95	3000	100	"	310	96.7	2.25	3.40
32	95	3000	90	"	330	97.0	2.40	3.51
33	95	3000	75	"	360	97.5	2.61	3.69
34	95	3000	700	.3 Wt.% Ca(OH)$_2$ Slurry	50	76.7	0.47	1.46
35	95	3000	575	"	70	80.8	0.66	1.65
36	95	3000	427	"	115	85.8	1.09	1.95
37	95	3000	300	"	160	90.0	1.52	2.30
38	95	3000	250	"	200	91.7	1.90	2.48
39	95	3000	200	"	250	93.3	2.38	2.71
40	95	3000	200	"	315	93.3	2.99	2.71
41	95	3000	190	"	355	93.7	3.38	2.76
42	95	3000	100	"	470	96.7	4.47	3.40
43	95	3000	2700	.4 Wt.% Ca(OH)$_2$ Slurry	38	10.0	0.44	0.10
44	95	3000	2000	"	60	33.3	0.70	0.41
45	95	3000	1975	"	82	34.2	0.96	0.42
46	95	3000	1800	"	105	40.0	1.23	0.51
47	95	3000	1475	"	125	50.8	1.47	0.71
48	95	3000	450	"	169	85.0	1.98	1.90
49	95	3000	250	"	212	91.7	2.49	2.48
50	95	3000	175	"	288	94.2	3.38	2.84
51	95	3000	110	"	370	96.3	4.35	3.31
52	95	3000	100	"	422	96.7	4.96	3.40
53	95	3000	2800	.5 Wt.% Ca(OH)$_2$ Slurry	40	6.7	0.56	0.07
54	95	3000	2000	"	87	33.3	1.21	0.41
55	95	3000	1500	"	130	50.0	1.82	0.69
56	95	3000	750	"	168	75.0	2.35	1.39
57	95	3000	560	"	240	81.3	3.36	1.68
58	95	3000	450	"	300	85.0	4.20	1.90
59	95	3000	350	"	368	88.3	5.15	2.15
60	95	3000	250	"	420	91.7	5.88	2.48

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* Standard Conditions: 32°F; 1 atm.

4.5.4 Analysis of Experimental Spray Tower Data

An equation which is commonly used to correlate vapor-liquid mass transfer data is given below.

$$K_G a = \frac{G}{PV} \cdot NTU \qquad (4\text{-}13)$$

where:

K_G = overall mass transfer coefficient, lb-moles/hr-ft^2-atm;

a = interfacial mass transfer area per unit scrubber volume, ft^2/ft^3;

G = scrubber vapor flow rate, lb-moles/hr;

P = scrubber operating pressure, atm;

V = scrubber volume, ft^3

NTU = number of overall gas-phase transfer units.

Actually, Equation 4-13 is obtained by integrating the following differential equation which describes the mass transfer process taking place inside a scrubber.

$$\frac{K_G aP}{G} dV = \frac{dy}{(y-y^*)} \qquad (4\text{-}14)$$

where:

y = mole fraction SO_2 in vapor phase,

y* = mole fraction SO_2 in vapor phase in equilibrium with liquid phase.

In order to integrate this relationship to obtain the form shown in Equation 4-13, it is necessary to assume that the value of the term $K_G aP/G$ does not vary with position inside the scrubber. For this case, the integrated form of Equation 4-14 becomes

$$\frac{K_G aPV}{G} = NTU = -\int_{y_{in}}^{y_{out}} \frac{dy}{(y-y^*)} \qquad (4\text{-}15)$$

A rigorous treatment of this equation requires that an expression for y^* as a function of y be known. For the case where y^* is negligibly small compared to y, the simplified form of the mass transfer equation shown below is obtained.

$$\frac{K_G aPV}{G} = \ln \frac{y_{in}}{y_{out}} = NTU \qquad (4\text{-}16)$$

In this analysis it has been assumed that there is negligible mass transfer back pressure ($y^* = 0$).

Because the physical properties of the different scrubbing liquors evaluated did not vary significantly, the performance characteristics of the spray nozzle used here should not have been noticeably affected by changes in scrubbing solution. At some given volumetric liquid flow rate, the interfacial mass transfer surface area (the "a" term in Equation 4-16) should have been reasonably constant for all of the solutions considered.

Because of this fact, the easiest way to compare the experimental results reported here is to plot the calculated NTU values shown in Table 4-5 as a function of the scrubber liquid flow rate. Since the values of G, P, V and a should all have remained reasonably constant at a given liquid rate as the scrubbing solution was varied, this method of analysis should reveal whether the presence of solid phase lime species significantly affected the value of K_G.

A plot of NTU as a function of the scrubber liquid rate is shown in Figure 4-25. The data shown in this figure are somewhat confusing. This is particularly true of the cases where the concentration of lime solids in the scrubbing liquor is greater than 0.3 wt.%. Presumably, these anomalies are due to liquid distribution problems which occurred as the concentration of solids in the scrubber liquid increased. In the runs in which lime slurries were evaluated, the small spray nozzle used sometimes became plugged with lime particles. The result of this was a non-uniform spray pattern within the scrubber (i.e., most of the liquid sprayed to one side). This could account for the unusual behavior of those curves shown in Figure 4-25 for which the lime solids content was greater than 0.3 wt.%. If these questionable experimental data are dropped from consideration, the result is the set of curves shown in Figure 4-26.

It can be seen from the data presented in Figure 4-26, that the rate of lime dissolution is apparently sufficiently large that it does influence the rate of SO_2 mass transfer in a short-residence time spray scrubber. As the wt.% solids content of the slurry was increased from 0 to 0.2 wt.%, a significant increase in the mass transfer rate was observed even though the initial soluble alkalinity entering the scrubber was the same in each case. It can be concluded from these results that lime particles which are $\approx$ 1 micron in diameter do dissolve rapidly enough to affect the sorption rate of SO_2 in a typical spray scrubber.

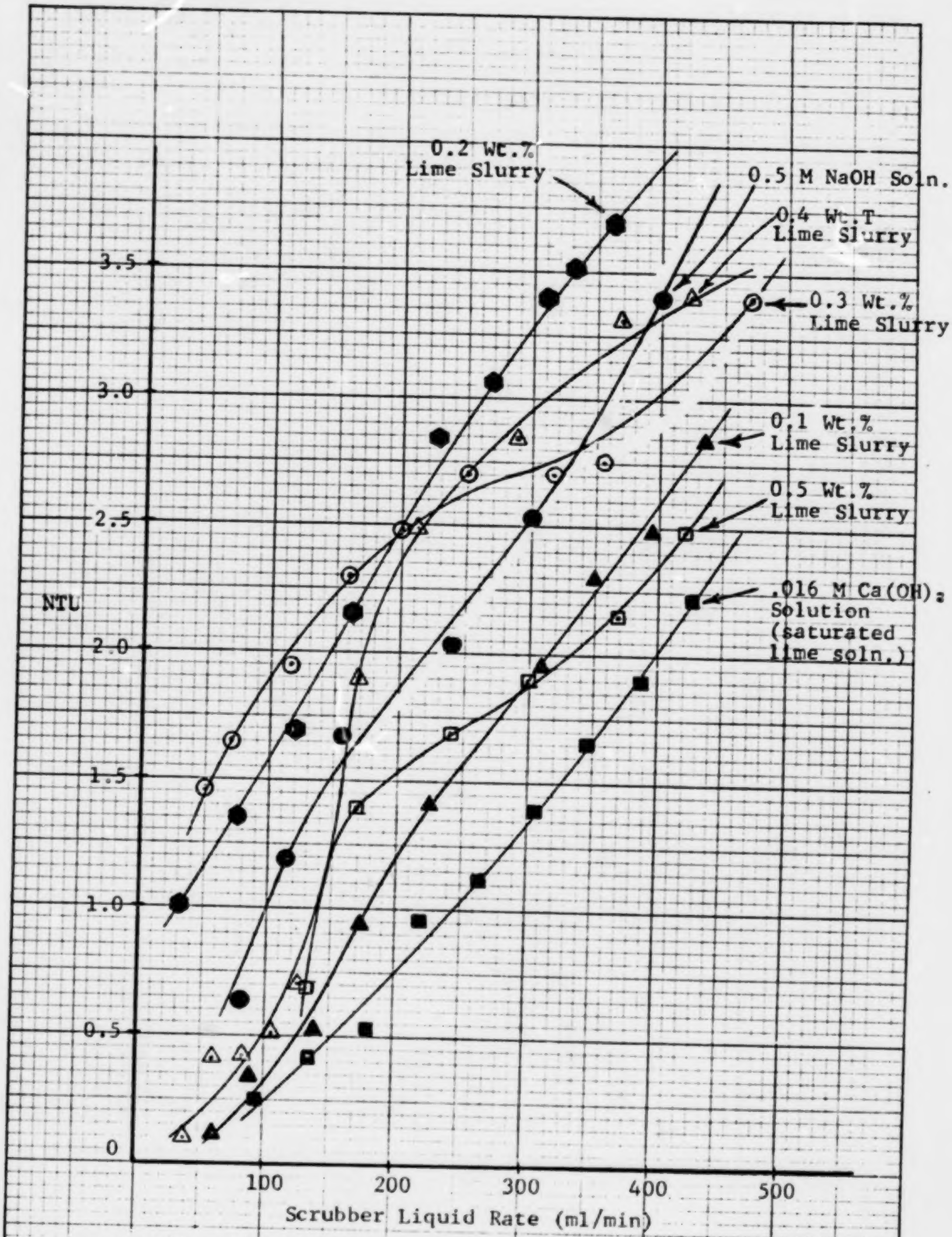


FIGURE 4-25 - GAS PHASE TRANSFER UNITS OBTAINED AS A FUNCTION OF THE SCRUBBER LIQUID FEED RATE

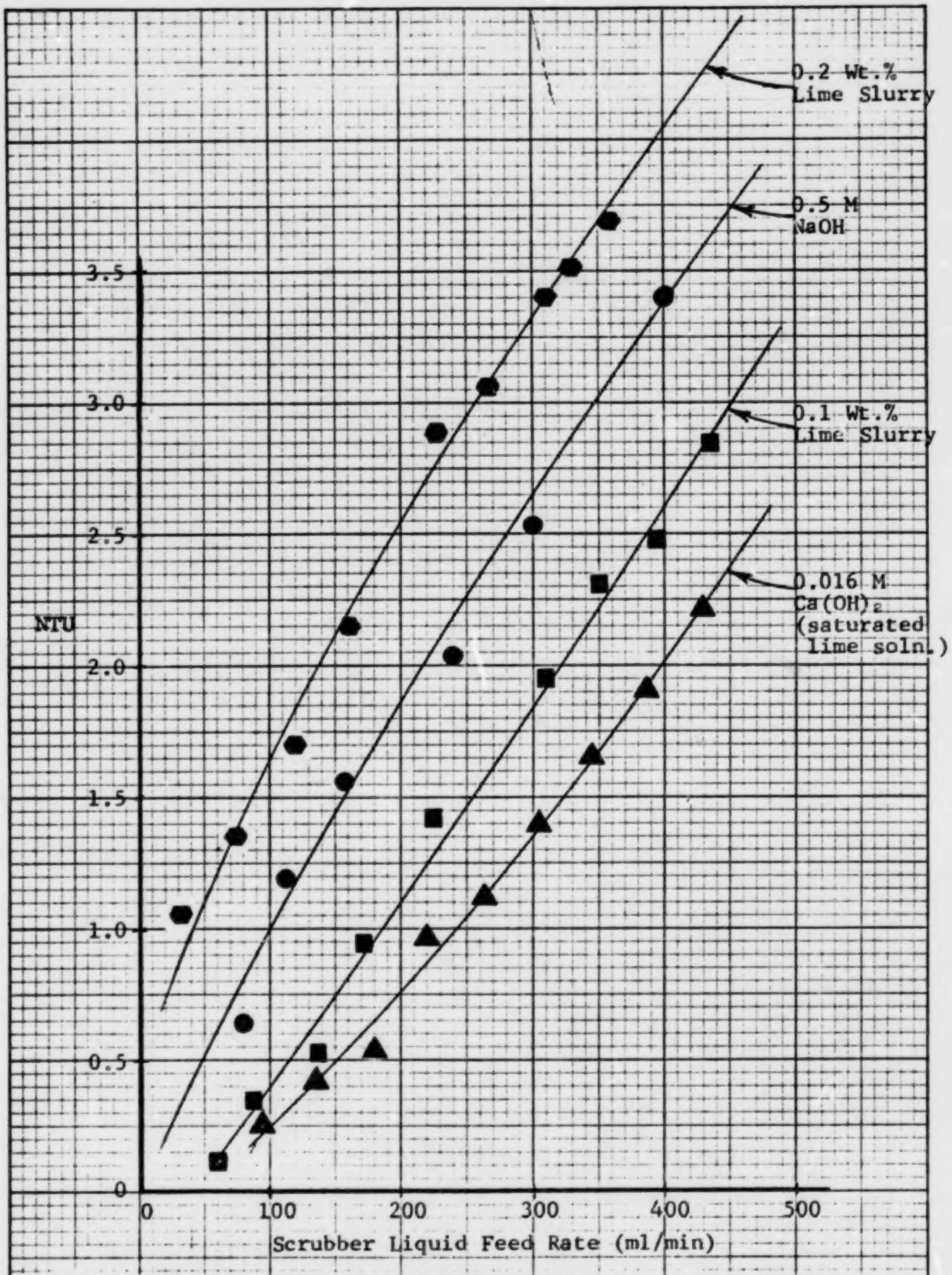


FIGURE 4-26- NTU VALUES OBTAINED FOR SCRUBBING LIQUORS CONTAINING < 0.3 WT.% SOLIDS

4.5.5 Conclusions

The major conclusions of this qualitative study of lime dissolution are:

- subject to equilibrium constraints, lime particles of a given size will dissolve faster in aqueous solutions than limestone particles of the same size.
- this intrinsic rate difference is often enhanced by the fact that lime particles are typically smaller than limestone particles. This is particularly true of commercially prepared lime and limestone samples.
- well-stirred process hold tanks containing solid phase hydrated lime can probably be assumed to be saturated with respect to $Ca(OH)_2$ in the liquid phase.
- the dissolution rate of a typical lime sample is so rapid that a significant contribution to the total alkalinity of the system can be expected to be supplied by lime species which initially enter a scrubber in the solid phase. The effects of this rapid dissolution rate should be taken into account whenever attempting to model or design a lime scrubbing system for SO_2 removal.

Although these experiments did not successfully quantify the dissolution rate of lime in aqueous solutions or the factors affecting that rate, they did serve to indicate the magnitude of the difference between lime and limestone dissolution rates. These observed rate differences could have a significant effect upon the relative performance characteristics of lime and limestone based SO_2 scrubbing systems.

5.0 SO_2 SCRUBBING TESTS AT THE WINDSOR PILOT FACILITY

To accelerate the commercial development of the lime/limestone wet scrubbing systems, EPA contracted Combustion Engineering to conduct research and development on pilot scale and prototype scale lime/limestone wet scrubbing systems. EPA contracted Radian Corporation to provide Combustion Engineering with technical support for their lime/limestone wet scrubbing research. Radian Corporation's primary responsibilities were:

(1) test program design,

(2) sampling and chemical analysis of process streams,

(3) engineering analysis and interpretation of test results,

(4) dynamic updating of the test program,

(5) recommendations for future tests,

(6) reporting the analysis of test results and describing their significance to EPA's limestone scrubbing demonstration program at TVA's Shawnee station.

This section of the final report reviews Radian Corporation's findings and conclusions evolved in support of Combustion Engineering's lime/limestone wet scrubbing tests at their pilot scale facilities in Windsor, Connecticut.

5.1 Windsor Pilot Test Unit

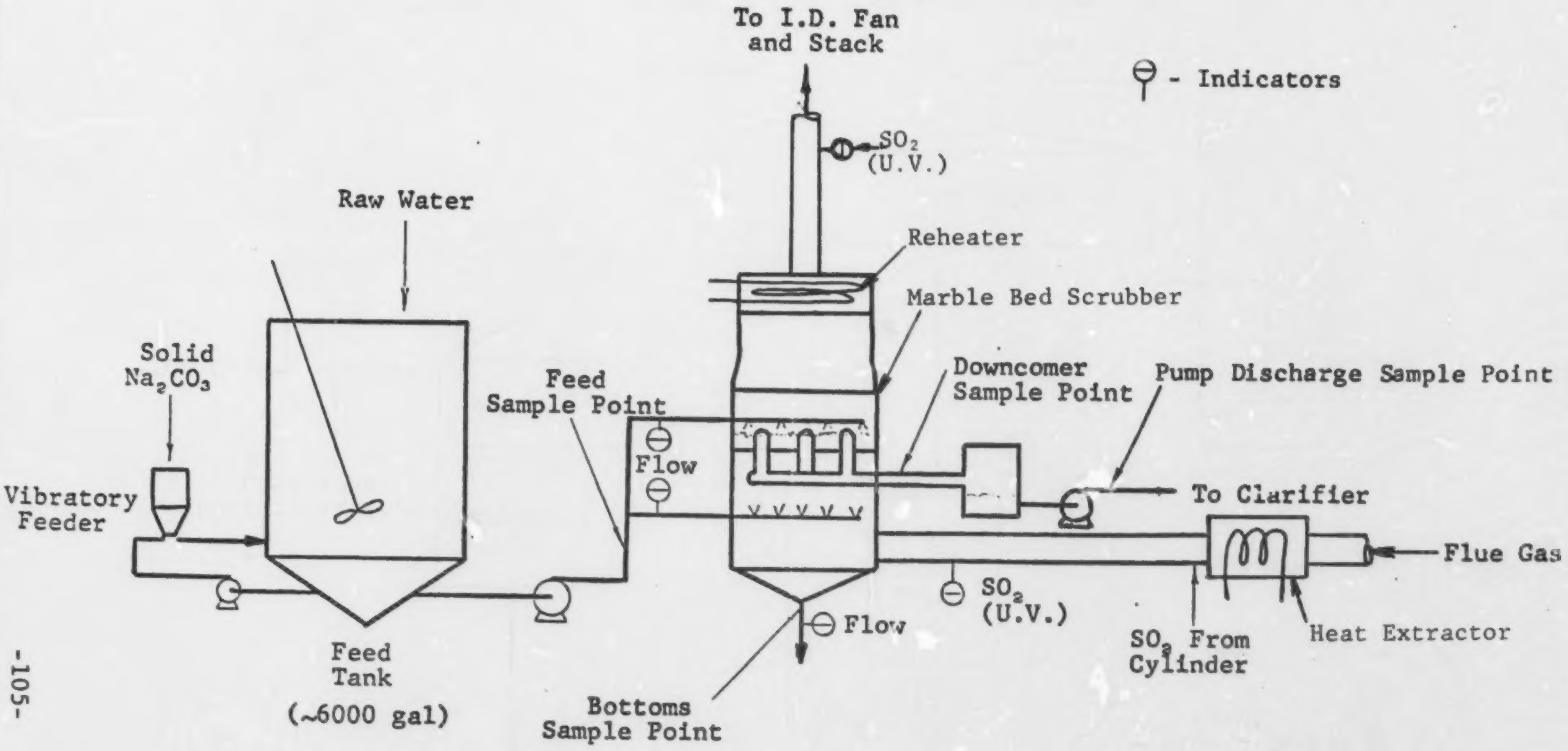
The lime/limestone wet scrubbing tests were performed at the Combustion Engineering pilot test facilities located at the Kreisinger Development Laboratory in Windsor, Connecticut. This pilot test unit was designed and built by Combustion Engineering and is similar to several of their field installations such as those at Kansas Power and Light and Kansas City Power and Light.

5.1.1 Equipment

The CE pilot test unit is basically of modular arrangement, designed to allow rapid system modifications and alterations. The piping and pumps are arranged to allow several different processing schemes. The five flow schemes utilized in the lime/limestone wet scrubbing test program are presented in Figures 5-1 through 5-3b.

The gas-liquid contactor used in the pilot tests was a 25 sq. ft. marble bed scrubber, constructed such that it could be altered from a single bed to a double bed scrubber. The piping of the marble bed scrubber was designed for above-bed and/or below-bed slurry sprays. Spent scrubbing slurry was withdrawn from the scrubber through the scrubber bottom and through downcomers in the marble bed.

Flue gas for the pilot tests was supplied by an oil-fired package boiler which had a flue gas output of 12,500 ACFM to 15,000 ACFM (measured at 14.7 psia and 125°F). A heat extractor before the scrubber and a reheater after the scrubber allowed variations in the inlet flue gas temperature to the scrubber. In order to simulate coal-fired boilers and boiler



To I.D. Fan and Stack
- Indicators
SO_2 (U.V.)
Raw Water
Reheater
Marble Bed Scrubber
Solid Na_2CO_3
Feed Sample Point
Downcomer Sample Point
Pump Discharge Sample Point
Vibratory Feeder
Flow
To Clarifier
Flue Gas
SO_2 (U.V.)
Flow
Heat Extractor
Feed Tank
(~6000 gal)
SO_2 From Cylinder
Bottoms Sample Point

FIGURE 5-1 - SCRUBBER SYSTEM FLOW SHEET - ONCE-THROUGH SOLUBLE Na_2CO_3 RUNS

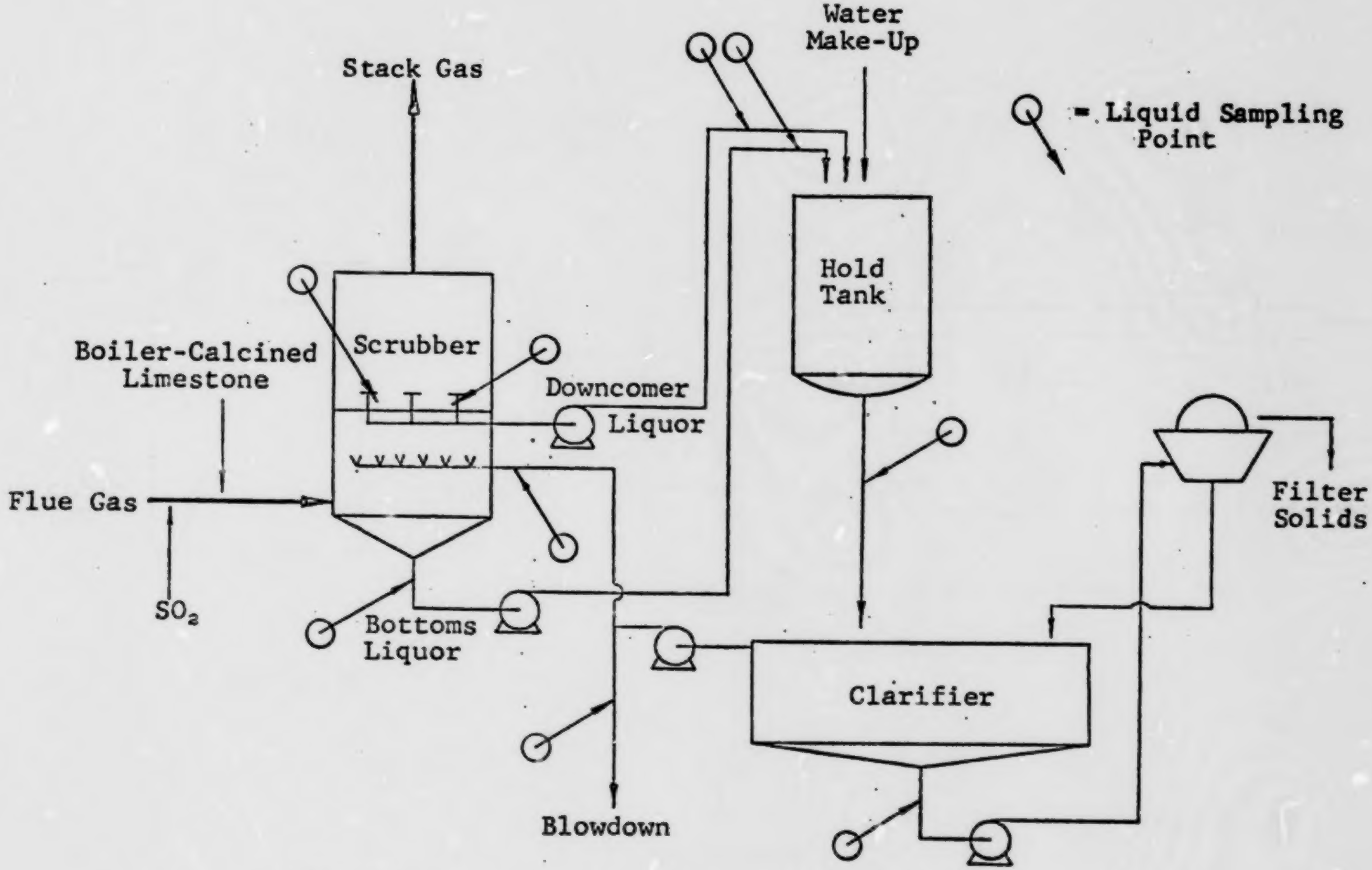

Stack Gas
Water
Make-Up
= Liquid Sampling Point
Hold
Tank
Scrubber
Boiler-Calcined
Limestone
Downcomer
Liquor
Flue Gas
SO_2
Bottoms
Liquor
Filter
Solids
Clarifier
Blowdown

FIGURE 5-2a - SCRUBBER SYSTEM FLOW SHEET FOR RUN 17R

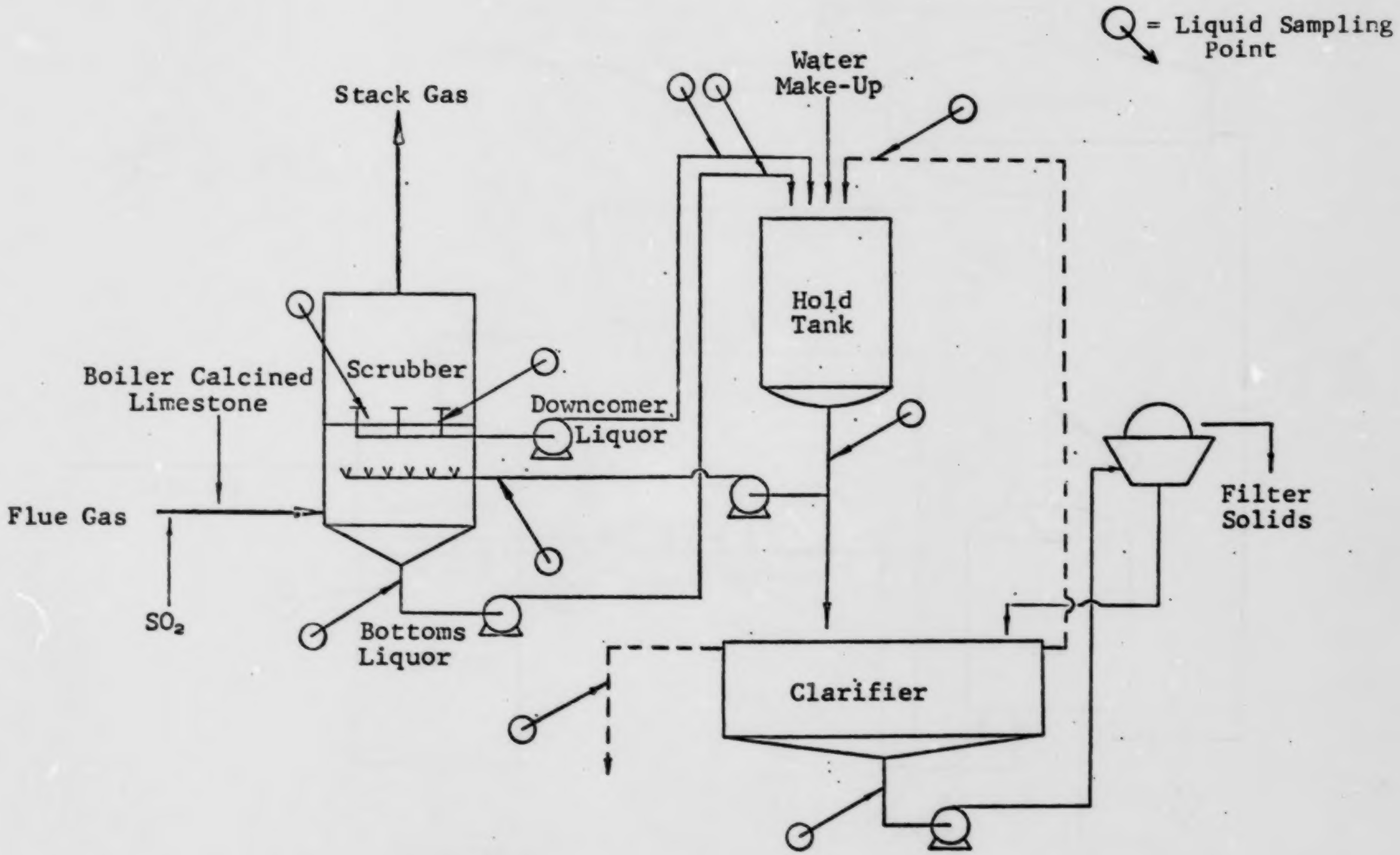

= Liquid Sampling Point
Stack Gas
Water Make-Up
Hold Tank
Scrubber
Boiler Calcined Limestone
Downcomer Liquor
Flue Gas
SO₂
Bottoms Liquor
Filter Solids
Clarifier

FIGURE 5-2b - SCRUBBER SYSTEM FLOW SHEET FOR RUNS 18R-22R

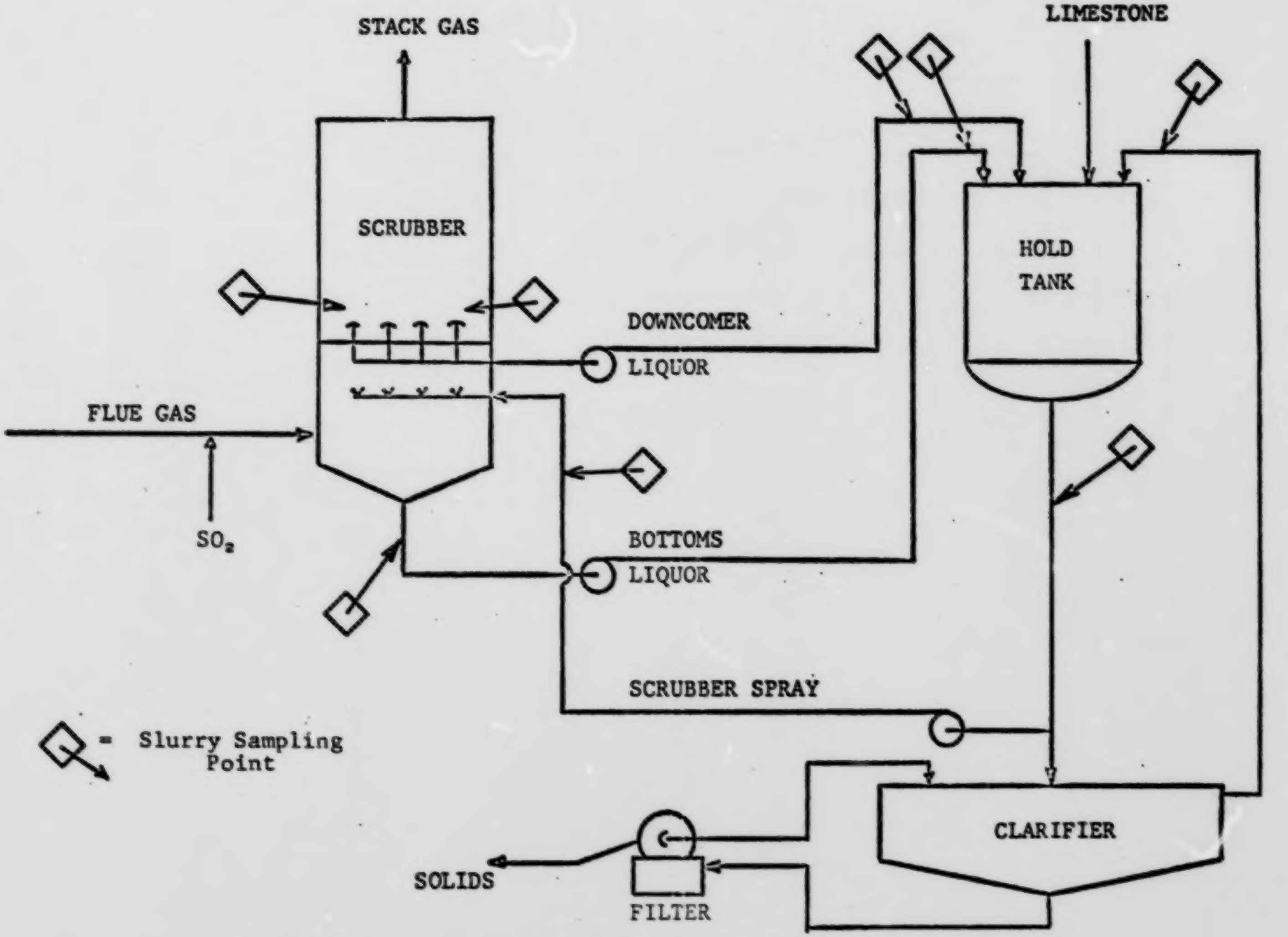

STACK GAS
LIMESTONE
SCRUBBER
HOLD
TANK
DOWNCOMER
LIQUOR
FLUE GAS
SO₂
BOTTOMS
LIQUOR
SCRUBBER SPRAY
= Slurry Sampling Point
CLARIFIER
SOLIDS
FILTER

FIGURE 5-3a - SCRUBBER SYSTEM FLOW SHEET FOR TAIL-END ADDITION TESTS (SINGLE BED)

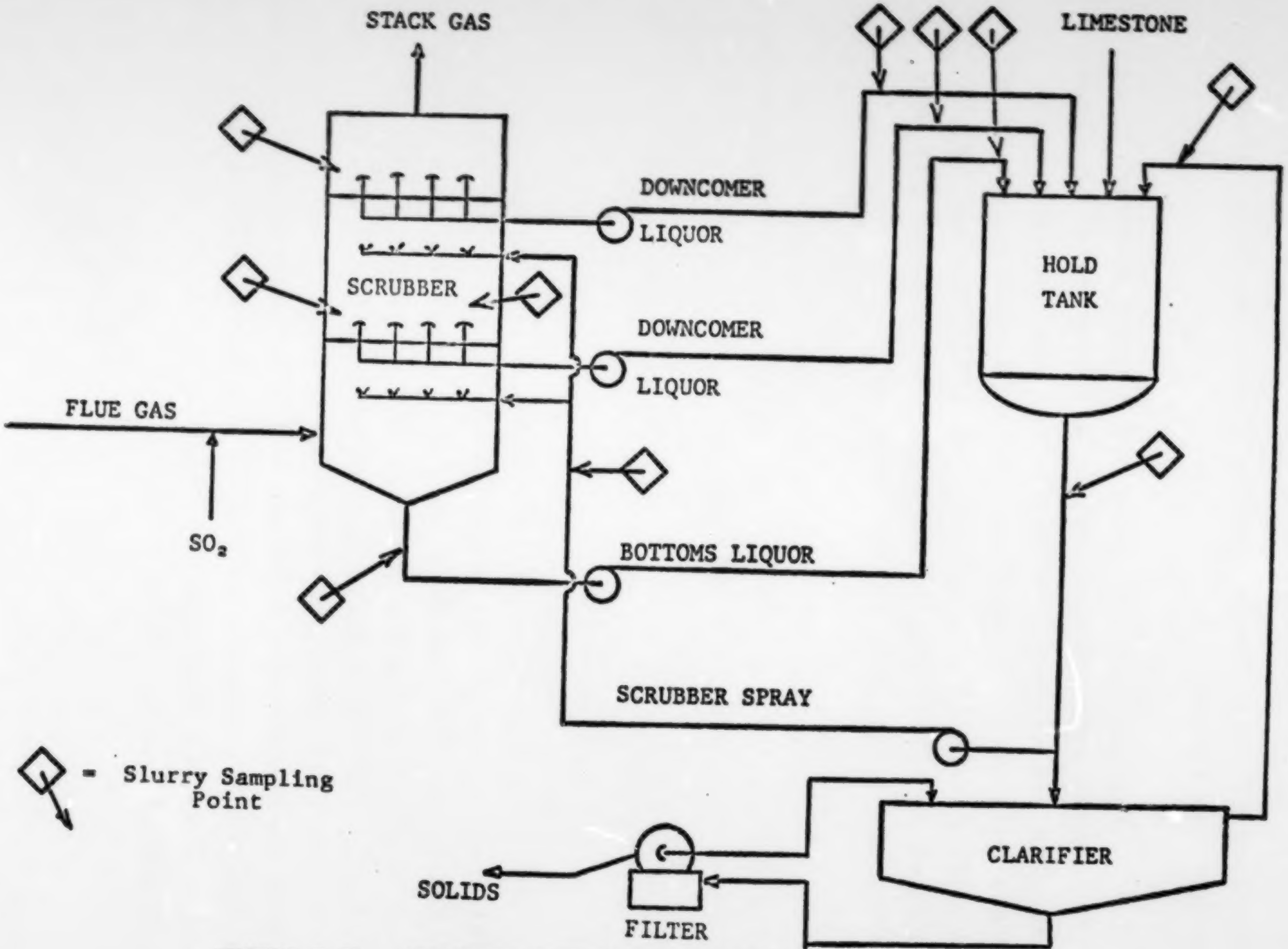

STACK GAS
LIMESTONE
DOWNCOMER
LIQUOR
HOLD
TANK
SCRUBBER
DOWNCOMER
LIQUOR
FLUE GAS
SO₂
BOTTOMS LIQUOR
SCRUBBER SPRAY
= Slurry Sampling Point
CLARIFIER
SOLIDS
FILTER

FIGURE 5-3b - SCRUBBER SYSTEM FLOW SHEET FOR TAIL-END ADDITION TEST (DOUBLE BED)

injected limestone scrubbing processes, an additive feeder was installed in the inlet flue gas system which fed metered quantities of coal fly ash and/or boiler calcined limestone into the flue gas stream.

The process hold tank had a maximum capacity of 6,000 gallons and was designed to allow operation at lower capacities. A variable speed stirrer was mounted on the process hold tank for keeping the solids suspended and the tank well mixed. There was also an additive feed system connected to the process hold tank which allowed the metered feeding of an additive to the hold tank.

The Combustion Engineering pilot unit also was equipped with a 20,000 gallon clarifier and a vacuum filter for dewatering clarifier sludge.

5.1.2 Instrumentation

The flow rate of the flue gas stream leaving the marble bed contactor was measured with a calibrated pitot tube and the inlet flue gas flow rate was calculated by accounting for a 7% air leak in the scrubber and a change in the flue gas humidity. The temperature and humidity of both the inlet and the outlet flue gases were measured using dry and wet bulb mercury thermometers. A DuPont 400 U.V. analyzer was used to measure the SO_2 concentrations of the inlet and the outlet flue gases. This SO_2 analyzer was calibrated before each test with a standard SO_2-air mixture.

The instrumentation for aqueous streams included magnetic flow meters for primary slurry flows. Pumps and valves were manually regulated.

5.1.3 Instrument Calibration

Two preliminary sodium carbonate tests were performed in August 1971 and calculations by Radian indicated a 30-40% error in the sulfur material balance. Recalibration of the liquid flow meters by Combustion Engineering showed that the liquid flow rates were about 12% larger than indicated.

Recalibration of the gas flow rate instruments and the discovery of several air leaks into the marble bed contactor accounted for the remaining sulfur material balance error.

These first two sodium carbonate tests were rerun using the recalibrated instrumentation.

5.1.4 Sampling and Analytical Procedures

The slurry sampling points utilized in each phase of the SO_2 scrubbing tests are indicated on the scrubbing flow schemes presented in Figures 5-1, 5-2a, 5-2b, 5-3a, and 5-3b. By use of a small laboratory pump, slurry samples were pumped from the sampling points to a central sampling bench. Representative temperature and pH measurements were taken by continuously pumping the slurry over the pH electrodes and the mercury thermometer. Slurry samples were taken for percent solids measurements. The slurry samples were also pumped through a 0.8 micron Millipore filter for the purpose of collecting solid samples and clear liquid samples.

Slurry sampling lines, sampling probes, and the sampling pump were sized and designed for collecting slurry samples as rapidly as feasible, minimizing changes due to chemical reactions. Because the marble bed liquor was not uniform over the scrubber cross section due to non-uniform gas distribution, downcomer slurry samples were taken from both sides of the marble bed and averaged.

The solids and liquor samples were chemically analyzed in Radian Corporation's laboratories using the procedures documented in Radian Final Report on EPA Contract CPA-70-143.

5.2 Test Program and Objectives

Radian Corporation designed the original test program for the Windsor lime/limestone wet scrubbing tests under EPA Contract CPA 70-45. The primary objectives of the test program were to:

(1) determine the rate limiting steps and their values in the lime/limestone wet scrubbing system. These rate steps include vapor-liquid mass transfer rates, solid-liquid mass transfer rates, and oxidation rates. The adequate determination of these rates is required to predict SO_2 removal as a function of process conditions and thus properly design lime/limestone wet scrubbing processes for the broad spectrum of control applications.

(2) assess the scaling problems created by handling supersaturated slurries.

(3) evaluate the sampling and analytical techniques developed by Radian for dealing with supersaturated slurries.

5.2.1 Phase I - Soluble Sodium Carbonate Tests

In order to efficiently attain the three primary objectives mentioned above, the Radian test program was divided into three phases. Phase I consisted of once-through flue gas scrubbing with a clear sodium carbonate scrubbing liquor. Since sodium carbonate is a highly soluble alkali scrubbing agent and its reaction products are soluble, the effects of slurries, crystallization, dissolution, and supersaturation were eliminated from the Phase I scrubbing tests. This allowed the Phase I scrubbing tests to concentrate on the following three points:

(1) What is the effect of major contacting variables on vapor-liquid mass transfer rates in a pilot scale marble bed?

(2) What is the approach to vapor-liquid equilibrium in a pilot scale marble bed?

(3) Is the vapor or liquid film resistance controlling?

The operating conditions of the 16 sodium carbonate scrubbing tests which comprised Phase I are listed in Table 5-1. In these Phase I tests the following contacting variables were manipulated to assess their relationship to the above three questions:

TABLE 5-1
SCRUBBER OPERATING CONDITIONS

Test No.	Date	Feed Composition (mmole/ℓ Na_2CO_3)	Liquor Temp.(°F)		Liquor Flow Rates (gpm)				Outlet Gas Flow Rate (cfm at 130°F)	Gas Dewpoint (°F)		Gas Temp.(°F)		SO_2 Concentration (ppm)	
			In	Out	Feed Above	Feed Below	Downcomer	Bottom		In	Out	In	Out	In	Out
1R: Set 1	10/29/71	10.30	111	120	54	107	149	19.5	10,960	117	112	232	123	2,020	880
Set 2		10.55	111	120	54	107	149	20.0	10,960			231	123	2,020	880
2R: Set 1	10/27/71	11.90	112	129	--	165	88	77	10,750	118	123	294	129	2,050	750
Set 2		11.55	111	129	--	165	85	80	10,800			292	129	2,030	760
3R: Set 1	10/14/71	11.45	52	105	--	170	160	15	11,200			318	102	2,095	860
Set 2		11.10	52	105	--	170	160	15							
4R: Set 1	10/28/71	-----	116	127	--	170.5	153	15.3	10,775	118	121	306	130	2,030	800
Set 2		10.70	117	129	--	170	150	15.5	10,800			309	130	2,030	790
5R: Set 1	11/02/71	12.05	102	120	55	106	150	14	12,980	117	120	298	122	2,275	1,020
Set 2		12.50	102	120	55	107	145	14	12,980			298	122		
6R: Set 1	11/02/71	13.15	115	125	55	110	135	29	9,180	122	121	304	127	2,050	480
Set 2		13.20	115	125	55	110	136	26	9,180			304	127		
7R: Set 1	11/03/71	12.85	112	122	69	152	185	34.5	11,240	116	123.5	291	122	2,000	450
Set 2		13.00	112	123	69	152	185	34.5	11,240			299	122	2,000	460
8R: Set 1	11/03/71	15.55	109	121	36	73	93	15.0	11,200	116	123.5	312	125		
Set 2		13.75	116	125	36	73	90	15.5	11,190			300	125	1,780	830
9R: Set 1	10/29/71	12.65	110	121	54.5	116	155	14.5	11,000	115	119	292	124	2,050	700
Set 2		13.05	110	121	54.0	116	155	14.5	10,910			295	124	2,010	730
10R: Set 1	11/09/71	12.90	110	120	53	112	153.6	9.9	10,680	114	120	302	120	1,980	540
Set 2		12.80	111	121	53	112	152.8	10.7	10,690			304	121	1,960	520
11R: Set 1	10/14/71	55.70	52	84	--	165	155	14.0	11,500			288	108	1,980	120
Set 2		59.25	52	84	--	165	160	13.0	11,400						
12R: Set 1	11/09/71	66.90	110	121	53.5	110	150	17	11,210	114	118	295	122	2,020	110
Set 2		67.70	110	121	53.0	110	150	17	11,200			295	122	1,980	110
13R: Set 1	11/04/71	17.40	111	119	54	110	153	16.5	11,330	116	123.5	298	122	2,050	380
Set 2		18.05	111	119	54	110	153	16.5	11,400			298	122	2,040	280
14R: Set 1	11/05/71	16.40	115	122	36	75	95	15	11,300	113	122	300	129	2,070	780
Set 2		16.25	115	122	36	75	95	14	11,360			299	128	2,040	780
15R: Set 1	11/05/71	17.10	111	120	55	110	145	16.5	12,980	115	118	302	120	2,040	500
Set 2		17.40	111	120	55	110	146.5	16.5	12,980			299	121	2,040	500
16R: Set 1	11/05/71	17.60	110	116	55.5	110	145	20	11,500	111	118	223	116	2,010	350
Set 2		18.85	109	114	55.5	110	145	20	11,500			222	115	2,020	350

- gas flow rate
- liquor spray rate above bed
- liquor spray rate below bed
- Na_2CO_3 concentration in the scrubbing liquor
- inlet flue gas temperature

Figure 5-1 is a diagram of the scrubbing flow scheme utilized in the Phase I tests. The results and conclusions obtained from these tests are discussed in Section 5.4 of this report.

5.2.2 Phase II - Limestone Injection Wet Scrubbing Tests

Phase II of the Radian test program was composed of six limestone injection/wet scrubbing tests with either slurry or clear liquid recycle. In the limestone injection/wet scrubbing process, finely ground limestone is injected into the boiler where it is calcined to CaO and partially reacts with SO_2 to form $CaSO_4$. The unreacted CaO, along with the $CaSO_4$, is entrained in the flue gas and hydrated down stream in the scrubber where it forms an alkali scrubbing medium.

The primary objectives chosen for the Phase II tests program were to:

(1) observe the rates at which the gaseous species (SO_2, CO_2, O_2) are transferred to or from the scrubber luquor,

(2) observe the rate at which a boiler-calcined limestone additive hydrates and dissolves in the scrubber liquor and in the hold tank liquor,

(3) observe the rates at which the solid waste products precipitate from the liquor,

(4) observe the rates and types of chemical reactions in the aqueous phase which determine the driving forces for the above three rate steps,

(5) determine the applicability of laboratory determined precipitation and dissolution rate expressions,

(6) confirm the vapor-liquid mass transfer correlations derived from the sodium carbonate scrubbing test data,

(7) establish the supersaturation limits for the scale-free operation of large scrubbing units.

(8) demonstrate the ability of Radian sampling and analytical techniques to characterize a supersaturated slurry stream.

Table 5-2 presents the pilot scrubbing unit operating conditions for the Phase II test series. The operating parameters which were varied in order to assess their relationship to the limestone injection/wet scrubbing system's performance include:

- additive stoichiometry (from 65% to 80%),
- percent solids in the scrubber spray (from 0 to 8.5),

TABLE 5-2
OPERATING CONDITIONS - LIMESTONE INJECTION/WET SCRUBBING TESTS

Test Number	17R	18R	19R	20R	21R (CE 24R)	22R (CE 23R)
Stoichiometry (%)	65	65	75	75	80	80
Outlet Gas Flow Rate (acfm at 130°F)	11,000	11,000	10,000	10,000	9,700-10,000	9,900
Approximate Percent Solids in Scrubber Spray	------	3.5	1.4	0.7	7.5	8.5
Liquid to Gas Ratio (gal/1000 acf)	10	18.5	20	20.5	20	36
Gas Temperature (°F):						
In	236	290	290	300	340	300
Out	125	125	112	115	120	120
Gas Dewpoint (°F):						
In	132	---	110	108	108	108
Out	123	---	105	110	115	115
SO_2 Concentration (ppm):						
In	1,500	1,500	1,880	1,950	2,000	2,020
Out	750	390	1,060	1,250	780-845	520-590
Liquor Flow Rates (gpm):						
Spray	110	205	200	205	200	355
Downcomer	90	180	175	180	180	260
Bottoms	25	30	20	20	20	95
Clarifier Feed	145	25	35	80	10	10
Clarifier Liquid Returned	110	25	---	40	10	10
Clarifier Bottoms	4	3	3	4	3	---
Make-Up Water	55	3	40	45	---	---
Blowdown	55	---	35	40	---	---
Hold Tank Volume (gal)	6,000	6,000	6,000	6,000	3,000	5,300

- liquid to gas ratio (from 10 to 36 gal/10^3 acf),
- inlet flue gas temperature (from 236°F to 340°F),
- SO_2 concentration in the inlet flue gas (from 1500 to 2020 ppm),
- system blowdown (from 0 to 55 gpm),
- hold tank volume (from 3000 to 6000 gal)

Figures 5-2a and 5-2b show the flow schemes used for these tests. The results and conclusions derived from the six limestone injection - wet scrubbing tests comprising Phase II are presented in Section 5.5 of this final report.

5.2.3 Phase III - Limestone Tail-End Addition Tests

Phase III of the lime/limestone wet scrubbing test program was composed of six limestone tail-end addition tests. Three tests used a single marble bed scrubber and three tests used a double marble bed scrubber. One objective of these tests was to permit extrapolation of single-bed data which had to be taken at Shawnee to predict double-bed operation. The limestone tail-end addition/wet scrubbing flow scheme (Figures 5-3a and 5-3b) was chosen for investigation because it too has proven to be one of the most promising SO_2 control systems currently being developed. In the limestone tail-end addition/wet scrubbing system, limestone provides the alkali scrubbing agent and is added to the scrubbing system in the hold tank. Part of the limestone not reacting in the hold tank is slurried to the marble bed scrubber where it dissolves and provides increased alkalinity for SO_2 removal.

The basic objectives in the Phase III limestone tail-end addition/wet scrubbing tests were to:

(1) observe the rates at which the limestone additive dissolves in the marble bed scrubber and in the hold tank,

(2) observe the rates at which the gaseous species (SO_2, CO_2, O_2) are transferred to or from a limestone based scrubbing liquor,

(3) observe the rates at which the solid waste products precipitate from a limestone based scrubbing liquor,

(4) observe the rates and types of chemical reactions in the aqueous phase of limestone scrubbing systems which determine the driving forces for the above rate steps,

(5) determine the applicability of laboratory determined precipitation and dissolution rate expressions,

(6) confirm the vapor-liquid mass transfer correlations derived from the sodium carbonate and limestone injection scrubbing test data,

(7) establish the supersaturation limits for the scale-free operation of large limestone scrubbing units.

Table 5-3 lists the operating conditions for the six limestone tail-end addition/wet scrubbing tests. The "B" series of scrubbing tests were double marble bed tests with the L/G per bed equivalent to the L/G per bed of their counterpart in the single marble bed "A" series tests. The additive stoichiometries of the "A" and "B" tests were varied in a similar fashion. For all six of the Phase III limestone tail-end addition tests, the flue gas rate was held at approximately 10,000 ACFM, the percent solids at approximately 7.5%, the inlet flue gas temperature at approximately 200°F, the inlet SO_2 concentration at approximately 2400 ppm, and the hold tank volume at approximately 6000 gal. The clarifier feed rate was varied from 10 to 15 gpm in the "A" tests and was held at 15 gpm for the "B" tests.

The results and conclusions obtained by Radian Corporation in the limestone tail-end addition tests are discussed in Section 5.6 of this final report.

5.3 Soluble Sodium Carbonate Test Results

This section of the final report presents the results and conclusions obtained by Radian Corporation in the Phase I soluble sodium carbonate wet scrubbing tests. The flow scheme and operating conditions utilized in these tests were presented in Figure 5-1 and Table 5-1.

5.3.1 Analytical Results

Results of the chemical analyses performed on liquor samples taken from each of the wet scrubbing process streams are presented in Table 5-4. The electroneutrality imbalances

TABLE 5-3
OPERATING CONDITIONS - LIMESTONE TAIL-END ADDITION TESTS

Test Number	1A	2A	3A	1B	2B	3B
Stoichiometry (mole percent based on inlet SO_2)	157	145	98	152	147	94
Outlet Gas Flow Rate (acfm at 130°F)	10220	10080	9930	10090	10300	10280
Approximate Percent Solids in Scrubber Spray	7.5	6.6	7.6	6.6	8.6	Sample Lost
Liquid to Gas Ratio (gal/1000 acf)	15	24	24	31	46	47
Gas Temperature (°F)						
In	220	183	212	194	217	212
Out	122	124	149	134	131	124
Gas Dew Point (°F):						
In	105	113	106	114	113	115
Out	118	120	122	127	126	122
SO_2 Concentration (ppm):						
In	2310	2505	2345	2410	2435	2375
Out	1110	1010	980	545	290	365
Liquor Flow Rates (gpm):						
Upper Bed						
Spray	---	---	---	150	225	235
Downcomer	---	---	---	110	175	180
Lower Bed						
Spray	150	240	243	160	245	250
Downcomer	135	180	185	170	205	215
Bottoms	15	60	58	30	90	90
Clarifier Feed	12	15	10	15	15	15
Clarifier Weir	12	14	10	15	15	15
Clarifier Bottoms	0	1	0	0	0	0
Makeup Water	≈0	≈0	≈0	≈0	≈0	≈0
Blowdown	0	0	0	0	0	0
Hold Tank Volume (gal)	6000	6000	6000	6000	6000	6000
Upper Bed pH	---	---	---	5.8	5.7	5.5
Lower Bed pH	5.4	5.1	5.3	5.7	5.5	5.2

TABLE 5-4

CHEMICAL ANALYSES OF CE SOLUBLE TEST SAMPLES

Experiment Number	Date	Sample Location	Concentrations in Millimole/Liter									pH low/high	Temperature (°C)	% Ion Imbalance
			Ca	Mg	Na	K	Total S	SO$_2$ *,+	CO$_2$	Cl	Total N			
1R: Set 1		Feed					0.2			0.64		10.30	43.8	+6.6
		Downcomer						16.35	2.95			5.20/5.50	49.4	+0.6/+0.6
		Pump Discharge	0.92	0.37	20.6		19.35			0.72				
		Bottom	0.91	0.38	21.1		17.5	15.8	5.64	0.52		5.65	48.8	+1.8
Set 2		Feed	0.71	0.37	21.1		0.2		11.6			10.30	43.8	+2.0
		Downcomer						14.95	3.03			5.10/5.28	49.4	+0.1/-0.3
		Pump Discharge			21.7		19.5							
		Bottom			21.5		18.1	15.8	6.11			5.92/6.00	48.8	+1.7/-2.3
2R: Set 1		Feed	0.98	0.38	23.8		0.2		14.4	0.47	0.38	10.38	44.4	+2.5
		Downcomer						17.3	4.36			5.90/6.05	53.9	-5.8/-4.7
		Pump Discharge	1.01	0.39	24.0	0.013	20.5			0.49	0.25			
		Bottom	0.88	0.38	24.2		20.6	14.6		0.49	0.26	5.95/6.05	53.9	-5.6/-4.9
Set 2		Feed			23.1		0.2		13.8			10.36	43.8	-1.5
		Downcomer						16.55	3.87			5.95/6.05	53.9	-4.2/-2.4
		Pump Discharge			23.7		20.							
		Bottom			23.4		20.7	15.5	3.45			5.9 /6.05	53.9	-5.5/-4.6
3R: Set 1		Feed	0.03	0.37	23.9		0.3	0.3	12.74	0.60		10.93	15.0	-2.5
		Downcomer	1.02	0.40	24.5		23.9	20.3	3.81	0.56		4.40/4.65	34.0	-2.0/-1.8
		Pump Discharge												
		Bottom	0.84	0.39	23.1		19.65	16.8	7.02	0.67		5.75/6.00	39.0	-3.2/-1.3
Set 2		Feed	0.32	0.37	22.2		0.4	0.4	11.16	0.63		10.90	16.0	+0.6
		Downcomer	1.35	0.41	23.9		23.5	23.5	3.82	0.59		3.68/4.0	34.0	+3.4/+3.7
		Pump Discharge												
		Bottom	1.05	0.41	22.4		19.8	19.8	6.59	0.60		5.62/5.9	39.0	+2.8

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* Values given for the downcomer location are an average of two downcomer samples.

+ SO$_2$ analyses done by CE except for Runs 3R and 11R.

TABLE 5-4 - CHEMICAL ANALYSES OF CE SOLUBLE TEST SAMPLES (cont.)

Experiment Number		Date	Sample Location	Concentrations in Millimole/Liter									pH low/high	Temperature (°C)	% Ion Imbalance
				Ca	Mg	Na	K	Total S	SO_4*,+	CO_3	Cl	Total N			
4R:	Set 1		Feed					0.2					10.3	44.6	+6.6
			Downcomer						18.15	2.12			3.75/5.29	53.3	+4.4/+4.9
			Pump Discharge	.91	.36	20.2		19.3							
			Bottom	.91	.37	20.5	0.013	17.2	15.1	5.37			5.9	52.2	-0.2
	Set 2		Feed	.91	.37	21.4		0.2		10.9			10.30	46.2	+5.5
			Downcomer						17.9	2.17			3.93/5.36	53.9	+2.7/+2.8
			Pump Discharge			20.9		19.6							
			Bottom			21.6		16.8	14.8	5.64			6.02	52.2	+1.3
5R:	Set 1		Feed	0.94	0.38	24.1		0.2		15.0	0.50		10.37	38.9	-3.0
			Downcomer						20.0	3.04	0.54		5.32/5.57	48.9	-2.0/-2.7
			Pump Discharge	0.98	0.39	24.5		23.6							
			Bottom	1.00	0.40	25.1	0.013	22.6	21.4	5.31	0.54		5.84	51.7	+0.1
	Set 2		Feed			25.0		0.2		14.7			10.38	38.6	-0.7
			Downcomer						20.2	6.54			5.3 /5.58	48.9	-1.3/-2.4
			Pump Discharge			24.5		23.3							
			Bottom			25.5		22.2	21.4	5.72			5.85	51.7	-1.3
6R:	Set 1		Feed	0.83	0.39	26.3		0.2		15.9	0.51		10.35	46.1	-3.1
			Downcomer						20.7	4.73			5.92/6.12	51.1	+0.7/-0.7
			Pump Discharge	0.98	0.39	26.5		22.6			0.50				
			Bottom	0.93	0.40	26.6		18.0	14.9	9.12	0.51		6.32/6.44	51.1	-1.9/-0.5
	Set 2		Feed			26.4		0.2		15.6			10.35	46.1	-2.1
			Downcomer						20.5	4.67			5.88/6.12	51.1	-0.9/-2.6
			Pump Discharge			26.2		23.1							
			Bottom			27.3		18.6	16.7	3.94			6.38/6.43	51.1	-3.5/-4.0

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* Values given for the downcomer location are an average of two downcomer samples.

+ SO_4 analyses done by CE except for Runs 3R and 11R.

TABLE 5-4 - CHEMICAL ANALYSES OF CE SOLUBLE TEST SAMPLES (cont.)

Experiment Number		Date	Sample Location	Concentrations in Millimole/Liter									pH low/high	Temperature (°C)	% Ion Imbalance
				Ca	Mg	Na	K	Total S	SO_3 *,+	CO_3	Cl	Total N			
7R:	Set 1		Feed	0.82	0.37	25.7		0.2		14.7	0.64		10.7	44.4	-5.5
			Downcomer						19.8	5.26			6.05/6.4	48.9	+5.0/+1.6
			Pump Discharge	0.95	0.38	26.6		20.0			0.51				
			Bottom	0.99	0.38	26.7		21.0	18.5	7.56	0.52		6.15/6.2	50.0	-1.4/-0.9
	Set 2		Feed			26.0		0.2		13.92	0.53		10.68	44.7	-2.2
			Downcomer						17.7	5.32			6.06/6.35	49.4	-3.2/+0.5
			Pump Discharge			25.2		19.1							
			Bottom			25.5		20.7	18.6	6.36			6.06/6.18	50.5	-1.1/0
8R:	Set 1		Feed	0.74	0.36	31.1		0.2		16.9			10.46	44.7	-0.1
			Downcomer						22.9	3.62			5.78/6.00	49.4	+8.1/+6.8
			Pump Discharge	0.92	0.37	33.5		24.1							
			Bottom	0.83	0.37	31.5		19.7	17.6	11.3			6.5	51.1	-0.2
	Set 2		Feed			27.5		0.2		15.9			10.38	46.6	-2.0
			Downcomer						21.8	3.57			5.56/5.65	51.6	-1.9/2.2
			Pump Discharge			27.7		25.6							
			Bottom			29.6		19.7	18.5	9.69			6.38	51.6	+1.2
9R:	Set 1		Feed	0.75	0.36	25.3		0.25		13.7	0.56		10.38	43.3	+1.5
			Downcomer						18.3	3.55			5.65/5.9	49.4	-0.6/-0.9
			Pump Discharge	0.92	0.37	25.2		22.1			0.51				
			Bottom	0.91	0.37	25.0	0.013	20.1	18.2	7.33	0.55		6.01	48.8	+0.2
	Set 2		Feed			26.1		0.25		13.7			10.38	43.3	+2.8
			Downcomer						18.1				5.45/5.84	49.4	+3.4/+3.2
			Pump Discharge			24.3		21.5		3.55					
			Bottom			25.0		19.4	18.7	6.23			5.98	48.8	+3.2

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* Values given for the downcomer location are an average of two downcomer samples.

+ SO_3 analyses done by CE except for Runs 3R and 11R.

TABLE 5-4 - CHEMICAL ANALYSES OF CE SOLUBLE TEST SAMPLES (cont.)

Experiment Number	Date	Sample Location	Concentrations in Millimole/Liter Ca	Mg	Na	K	Total S	SO_4 *,+	CO_3	Cl	Total N	pH low/high	Temperature (°C)	% Ion Imbalance
10R: Set 1		Feed	0.96	0.39	25.8		0.2		15.8			10.35	43.3	-2.9
		Downcomer						20.1	5.37			5.62/5.8	48.9	+0.6/-0.4
		Pump Discharge	2.88	0.43	26.2		24.4							
		Bottom	1.81	0.39	26.3		22.2	20.4	5.19					+1.3/+2.5
Set 2		Feed			25.6		0.2		15.2			10.32	49.2	-2.1
		Downcomer						19.6	3.59			5.65/5.85	47.6	-1.9/-2.8
		Pump Discharge			26.4		23.8							
		Bottom			26.2		22.6	19.9	4.69			5.95/6.08	49.44	-1.8/-0.9
11R: Set 1		Feed	0.18	0.35	111.4		0.43		59.27	0.65	0.44	11.45	14.5	-3.4
		Downcomer	0.47	0.36	109.5		36.9	33.9	46.26	0.65	0.36	7.2 / 7.4	34.0	+0.1/+1.8
		Pump Discharge												
		Bottom	0.53	0.38	110.6		37.5	32.0	43.34	0.67	0.39	7.55/7.8	37.0	-1.1/+0.1
Set 2		Feed	.04	0.30	118.5		0.3		57.59	0.65		11.44	15.0	+1.5
		Downcomer	.49	0.36	114.7		37.55	36.0	53.96	0.66		7.28/7.5	34.5	-1.4/+0.3
		Pump Discharge												
		Bottom	.48	0.36	117.1		39.9	34.6	52.80	0.63		7.25/7.5	37.0	-2.0/-0.2
12R: Set 1		Feed	1.30	0.37	133.8	0.013	0.2		66.5		0.44	10.77	43.6	+1.5
		Downcomer						28.7	65.9			7.78/8.02	49.4	-3.0/+2.1
		Pump Discharge	0.18	0.36	133.1	0.012	30.8				0.32			
		Bottom	0.21	0.36	135.4	0.013	34.6	34.1	64.8		0.47	7.62/7.75	50.0	+2.0/+2.7
Set 2		Feed			135.4		0.2		67.8			10.75	43.3	+1.2
		Downcomer						28.1	68.3			7.97/8.15	49.4	+1.5/+0.9
		Pump Discharge			133.2		30.8							
		Bottom			133.6		34.1	32.9	65.1			7.82/7.95	50.5	+0.9/+1.4

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* Values given for the downcomer location are an average of two downcomer samples.

+ SO_4 analyses done by CE except for Runs 3R and 11R.

TABLE 5-4 - CHEMICAL ANALYSES OF CE SOLUBLE TEST SAMPLES (cont.)

Experiment Number	Date	Sample Location	Ca	Mg	Na	K	Total S	SO_4*,+	CO_3	Cl	Total N	pH low/high	Temperature (°C)	% Ion Imbalance
			Concentrations in Millimole/Liter											
13R: Set 1		Feed	0.86	0.35	34.8		0.2		19.1			10.48	42.6	-0.3
		Downcomer						24.2	5.04			5.95/6.22	48.6	-0.1/-2.1
		Pump Discharge	0.85	0.36	33.6		27.8							
		Bottom	0.70	0.37	34.8		25.3	22.0	9.96			6.4	48.9	-2.6
Set 2		Feed			38.1		0.2		19.9			10.52	42.6	+1.4
		Downcomer						25.0	6.73			6.08/6.35	48.3	-1.6/-4.2
		Pump Discharge			32.8		27.6							
		Bottom			40.4		26.3	23.1	11.9			6.43	48.9	0.0
14R: Set 1		Feed	1.11	0.39	32.8		0.2		19.4			10.37	46.1	-2.0
		Downcomer						26.6	3.80			5.63/5.87	50.0	-0.6/-1.7
		Pump Discharge	1.02	0.40	33.6		30.4							
		Bottom	0.61	0.40	34.6		22.8	21.2	12.5			6.48/6.55	50.0	-2.3/-1.3
Set 2		Feed			32.5		0.2		18.[illegible]			10.37	46.1	- -0.2
		Downcomer						25.6	4.71			5.72/5.81	50.0	-2.8/-3.3
		Pump Discharge			33.9		30.6							
		Bottom			33.6		22.0	20.2	12.7			6.5	50.0	-1.9
15R: Set 1		Feed	0.87	0.39	34.2		0.2		20.0			10.38	43.6	-1.8
		Downcomer						26.1	5.03			5.42/6.18	48.9	+2.1/+2.0
		Pump Discharge	0.97	0.40	35.2		29.7							
		Bottom	0.91	0.40	35.0		28.2	25.7	8.54			6.33	48.9	-3.0
Set 2		Feed			34.8		0.2		20.1			10.38	43.6	-1.2
		Downcomer						25.8	5.58			5.96/6.25	48.9	-0.6/-2.9
		Pump Discharge			35.1		29.5							
		Bottom			35.1		27.8	25.4	8.90			6.23	49.2	-1.5

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* Values given for the downcomer location are an average of two downcomer samples.

+ SO_4 analyses done by CE except for Runs 3R and 11R.

TABLE 5-4 - CHEMICAL ANALYSES OF CE SOLUBLE TEST SAMPLES (cont.)

Experiment Number	Date	Sample Location	Concentrations in Millimole/Liter									pH low/high	Temperature (°C)	% Ion Imbalance
			Ca	Mg	Na	K	Total S	SO_2*,+	CO_2	Cl	Total N			
16R: Set 1		Feed	0.84	0.39	35.2		0.2		19.8			10.38	41.8	-1.3
		Downcomer						24.9	5.72			6.03/6.42	46.3	+0.4/-3.3
		Pump Discharge	1.15	0.40	34.9	0.014	28.3							
		Bottom	0.91	0.40	35.4		25.6	18.8	11.3			6.37/6.45	46.5	-6.0/-5.1
Set 2		Feed			37.7		0.2		19.6			10.38	41.8	+3.4
		Downcomer						24.1	6.73			6.02/6.35	45.5	-0.1/-3.1
		Pump Discharge			36.2		28.5							
		Bottom			36.0		25.3	22.5	12.2			6.44/6.55	46.13	-4.1/-2.6

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* Values given for the downcomer location are an average of two downcomer samples.

+ SO_2 analyses done by CE except for Runs 3R and 11R.

calculated for each chemical analysis are included in this table. The percentage values shown are a ratio of the charge imbalance to the total equivalents of charged species analyzed for a given sample. This percentage is a measure of the accuracy of the liquid phase chemical analyses. In general the percentage imbalance has been less than 5% in previous work of this type. All of the data sets for the sodium carbonate tests except Runs 2R1 and 8R1 have resulted in a reasonable charge balance. Further discussion of this subject is given in Radian Technical Note 200-014-05.

As a further check on the accuracy of the sampling and analytical techniques total sulfur material balances were performed around the scrubbing system. The results are presented in Table 5-5. The gas and liquid phase Δ sulfur terms were calculated from the relationship:

$$\Delta S = (\Sigma_{in} \text{ flow x concentration}) - (\Sigma_{out} \text{ flow x concentration}) \qquad (5\text{-}1)$$

The results were well within expected experimental error (<4%) for all runs except 3R. Further discussion of this subject is given in Radian Technical Note 200-014-05.

5.3.2 Vapor-Liquid Mass Transfer Rates

From the chemical analysis of the downcomer stream, vapor-liquid equilibrium calculations were made for the marble bed scrubber in each test using an updated version of the Radian-developed chemical equilibrium program. Comparison of actual SO_2 concentrations in the gas leaving the scrubber with

TABLE 5-5

TOTAL SULFUR MATERIAL BALANCE

Run No.		Gas Out (gmole/min)	SO$_2$ Out (ppm)	Gas In (gmole/min)	SO$_2$ In (ppm)	ΔS Gas (gmole/min)	Liquid In (gpm)	Total S In (mmole/ℓ)	Liquid Out Bottom (gpm)	Total S Bottom (mmole/ℓ)	Liquid Out Downcomer (gpm)	Total S Down (mmole/ℓ)	ΔS Liquid (gmole/min)
1R:	Set 1	11,550	880	10,930	2,020	11.9	161	0.2	19.5	17.5	149	19.35	12.1
	Set 2	11,550	880	10,930	2,020	11.9	161	0.2	20.0	18.1	149	19.50	12.2
2R:	Set 1	11,340	750	10,390	2,050	12.8	165	0.2	77.0	20.6	88	20.50	12.7
	Set 2	11,390	760	10,440	2,030	12.5	165	0.2	80.0	20.7	85	20.00	12.6
3R:	Set 1	11,820	860	10,820	2,095	12.5	170	0.3	15.0	19.65	160	23.9	15.4
	Set 2	11,820	860	10,820	2,095	12.5	170	0.4	15.0	19.8	160	23.5	15.1
4R:	Set 1	11,370	800	10,485	2,030	12.2	170.5	0.2	15.3	17.2	153	19.3	12.0
	Set 2	11,390	790	10,510	2,030	12.3	170	0.2	15.5	16.8	150	19.6	12.0
5R:	Set 1	13,690	1,020	12,630	2,275	14.8	161	0.2	14.0	22.6	150	23.6	14.5
	Set 2	13,690	1,020	12,630	2,275	14.8	162	0.2	14.0	22.2	145	23.3	13.8
6R:	Set 1	9,685	480	9,070	2,050	13.9	165	0.2	29.0	18.0	135	22.6	13.4
	Set 2	9,685	480	9,070	2,050	13.9	165	0.2	24.0	18.6	136	23.1	13.4
7R:	Set 1	11,860	450	10,760	2,000	16.2	221	0.2	34.5	21.0	185	20.0	16.6
	Set 2	11,860	460	10,760	2,000	16.1	221	0.2	34.5	20.7	185	19.1	15.9
8R:	Set 1	11,820	830	10,720	1,780	9.3	109	0.2	15.0	19.7	93	24.1	9.5
	Set 2	11,805	830	10,710	1,780	9.3	109	0.2	15.5	19.7	90	25.6	9.8
9R:	Set 1	11,605	700	10,670	2,050	13.8	170.5	0.25	14.5	20.1	155	22.1	13.9
	Set 2	11,510	730	10,590	2,010	12.9	170.5	0.25	14.5	19.4	155	21.5	13.5
10R:	Set 1	11,270	540	10,290	1,980	14.3	165	0.2	9.9	22.2	153.6	24.4	14.9
	Set 2	11,280	520	10,300	1,960	14.3	165	0.2	10.7	22.6	152.8	23.8	14.5
11R:	Set 1	12,130	120	11,620	1,980	21.5	165	0.43	14.0	37.5	155	36.9	23.3
	Set 2	12,030	120	11,530	1,980	21.4	169	0.30	13.0	39.9	160	37.55	24.5
12R:	Set 1	11,830	110	10,890	2,020	20.6	163.5	0.2	17.0	34.6	150	30.8	19.6
	Set 2	11,820	110	10,880	1,980	20.2	163.5	0.2	17.0	34.1	150	30.8	19.5
13R:	Set 1	11,950	380	10,850	2,050	17.7	164	0.2	16.5	25.3	153	27.8	17.5
	Set 2	12,030	280	10,910	2,040	18.9	164	0.2	16.5	26.3	153	27.6	17.5
14R:	Set 1	11,920	780	10,780	2,070	13.0	111	0.2	15.0	22.8	95	30.4	12.1
	Set 2	11,985	780	10,840	2,040	12.8	111	0.2	14.0	22.0	95	30.6	12.1
15R:	Set 1	13,690	500	12,640	2,040	18.9	165	0.2	16.5	28.2	145	29.7	17.9
	Set 2	13,690	500	12,640	2,040	18.9	165	0.2	16.5	27.8	146.5	29.5	18.0
16R:	Set 1	12,130	350	11,090	2,010	18.0	165.5	0.2	20.0	25.6	145	28.3	17.3
	Set 2	12,130	350	11,090	2,020	18.1	165.5	0.2	20.0	25.3	145	28.5	17.4

equilibrium SO_2 concentrations for the liquor gives a measure of the vapor-liquid mass transfer capability of the scrubber.

In these calculations the marble bed scrubber was assumed to be a well mixed contactor with respect to the liquid phase. Because the bed composition is known to vary from side to side, two cases were considered for each data set. These used the highest and lowest measured pH values as inputs, giving a range of the highest and lowest equilibrium SO_2 partial pressures for each data set.

Results are presented in Table 5-6. The "relative overall mass transfer coefficients" listed in the right hand column are based upon the following relationship:

$$K_g a = \frac{G}{V} \ln \left(\frac{y_{SO_2 in} - y^*}{y_{SO_2 out} - y^*} \right) \qquad (5\text{-}2)$$

where G is the gas flow rate and y^* is the partial pressure of SO_2 in equilibrium with the marble bed calculated from the chemical analysis of the liquor. Normally V is the volume of the agitated layer in the marble bed, but because of the difficulties encountered in determining this volume, a V was arbitrarily chosen based upon the $K_g a$ of Test 9R being set equal to 1.0. Therefore, reported $K_g a$'s are all relative to the $K_g a$ of Test 9R (Set 1).

The percent approach to equilibrium shown in Table 5-6 was determined by:

TABLE 5-6

VAPOR LIQUID EQUILIBRIUM CALCULATIONS FOR Na_2CO_3 TESTS

Run No.		Experimental SO_2 (ppm) Out	Experimental SO_2 (ppm) In	Equilibrium SO_2 (ppm) low/high	Liquor pH low/high	% Approach to Equilibrium	Relative Overall Mass Transfer Coefficient low/high
1R:	Set 1	880	2,020	9/20	5.2 /5.5	55	0.8/0.8
	Set 2	880	2,020	15/24	5.1 /5.28	55	0.8/0.8
2R:	Set 1	750	2,050	3/5	5.9 /6.05	65	0.9/0.9*
	Set 2	760	2,030	3/4	5.95/6.05	65	0.9/0.9
3R:	Set 1	860	2,095	40/71	4.4 /4.65	60	0.9/0.9**
	Set 2	860	2,095	210/430	3.68/4.0	65/75	1.0/1.3**
4R:	Set 1	800	2,030	20/750	3.75/5.29	60/95	0.9/3.0*
	Set 2	790	2,030	20/510	3.93/5.36	60/80	0.9/1.5
5R:	Set 1	1,020	2,275	10/18	5.32/5.57	55	0.9/0.9
	Set 2	1,020	2,275	10/19	5.30/5.58	55	0.9/0.9
6R:	Set 1	480	2,050	3/5	5.92/6.12	75	1.1/1.1
	Set 2	480	2,050	3/5	5.88/6.12	75	1.1/1.1
7R:	Set 1	450	2,000	1/3	6.05/6.4	75	1.4/1.4
	Set 2	460	2,000	1/3	6.06/6.35	75	1.4/1.4
8R:	Set 1	830	1,780	4/7	5.78/6.0	55	0.7/0.7*
	Set 2	830	1,780	10/12	5.56/5.65	55	0.7/0.7
9R:	Set 1	700	2,050	4/8	5.65/5.9	65	1.0/1.0
	Set 2	730	2,010	4/12	5.45/5.84	65	0.9/0.9
10R:	Set 1	540	1,980	5/8	5.62/5.8	75	1.2/1.2
	Set 2	520	1,960	4/7	5.65/5.85	75	1.2/1.2
11R:	Set 1	120	1,980	0	7.2 /7.4	95	2.7/2.7
	Set 2	120	1,980	0	7.28/7.5	95	2.7/2.7
12R:	Set 1	110	2,020	0	7.78/8.02	95	2.7/2.7
	Set 2	110	1.980	0	7.97/8.15	95	2.7/2.7
13R:	Set 1	380	2,050	2/5	5.95/6.22	80	1.6/1.6
	Set 2	280	2,040	2/3	6.08/6.35	85	1.9/1.9
14R:	Set 1	780	2,070	6/12	5.63/5.87	65	0.9/0.9
	Set 2	780	2,040	7/9	5.72/5.81	60	0.9/0.9
15R:	Set 1	500	2,040	3/18	5.42/6.18	75	1.5/1.6
	Set 2	500	2,040	2/5	5.96/6.25	75	1.5/1.5
16R:	Set 1	350	2,010	1/3	6.03/6.42	85	1.7/1.7
	Set 2	350	2,020	1/3	6.02/6.35	85	1.7/1.7

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* The electroneutrality imbalance for these cases was unacceptable.

** The material balance for these cases was unacceptable.

$$\% = \frac{y_{SO_2 in} - y_{SO_2 out}}{y_{SO_2 in} - y^*_{SO_2}} \times 100 \qquad (5\text{-}3)$$

The data given in Table 5-6 indicate that the mass transfer capability of the marble bed scrubber is most strongly dependent on the liquor pH. The operating variables of flue gas temperature, liquor temperature, and gas velocity do not appear to have as significant an effect on relative mass transfer as do liquor flow rate and sodium carbonate concentration. The effect of liquor flow rate appears to be more consistent with changes in liquid film resistance rather than interfacial area for mass transfer.

Figure 5-4 is a plot of relative mass transfer coefficients vs. pH for the soluble sodium carbonate tests. The trends exhibited in this graph seem to indicate a direct relationship between downcomer liquor pH and the relative mass transfer rate.

5.3.3 Conclusions

From the results obtained in the soluble sodium carbonate tests the following conclusions were drawn:

(1) The liquor sampling and analytical techniques applied were adequate to investigate chemical processes occurring in soluble sodium carbonate/wet scrubbing systems.

(2) A vapor-liquid equilibrium approach of 95% can be obtained in single marble bed with a high pH sodium carbonate scrubbing liquor.

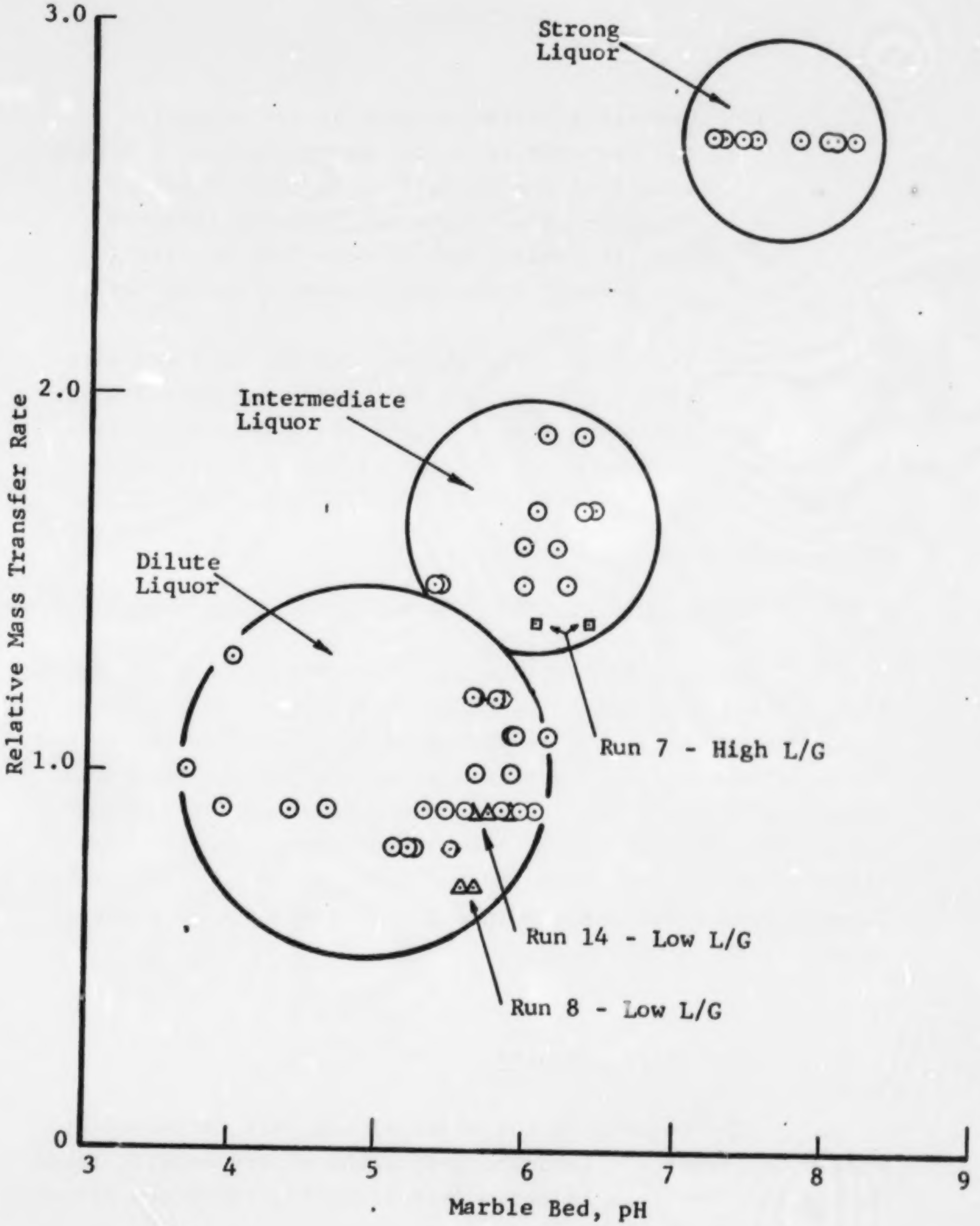

FIGURE 5-4 - RELATIVE MASS TRANSFER RATE VS. pH FOR SOLUBLE TEST

(3) Operating variables such as gas velocity and temperature do not appear to have a strong effect on the overall vapor-liquid mass transfer rate. This may indicate that the gas film mass transfer rate does not limit the overall vapor-liquid mass transfer rate.

(4) The correlation between overall mass transfer rate and liquor pH exhibited in Figure 5-4 indicates that a liquid phase resistance is a substantial portion of the overall vapor-liquid mass transfer resistance.

5.4 Limestone Injection Wet Scrubbing Tests

This section of the final report presents the results and conclusions obtained by Radian Corporation in the Phase II limestone injection/wet scrubbing tests. The flow sheets and operating conditions for these tests have been presented in Figures 5-2a and 5-2b. Because the Combustion Engineering boiler was not designed to allow limestone injection, limestone which had been injected and calcined in a Union Electric Company boiler was metered into the flue gas stream above the pilot scrubbing unit.

5.4.1 Analytical Results

The results of the chemical analysis performed by Radian Corporation's laboratories on the slurry samples taken during the limestone injection/wet scrubbing tests are presented in Appendix D of this report.

These analytical results again include the electroneutrality imbalances calculated by the Radian equilibrium computer program for each slurry sample analysis. Most of the analyses for the limestone injection tests have reasonable charge imbalances, i.e. less than 5%. There were consistently higher electroneutrality imbalances in the marble bed and scrubber bottom analyses which were due to sampling problems.

As a further check on the accuracy of both the sampling and the analytical techniques employed in the limestone injection tests, total sulfur material balances were performed around the scrubbing system. The results of these calculations are summarized in Table 5-7. The material balance errors were within 10% for the marble bed and within 5% for the hold tank. The marble bed errors were attributed to local variations in bed composition and to sampling problems. A brief discussion of the sampling technique employed at Windsor and their impact upon the accuracy of the analytical results is given below.

Successful characterization of a slurry scrubbing process depends upon the representativeness of samples taken from unstable process streams. A previously developed procedure was used to obtain rapid separation of solid and liquid phases during slurry sampling (see Radian Final Report on EPA Contract CPA-70-143). A sample was pumped directly from each process stream into a Millipore filter holder with a one micron pore size membrane. The sampling rate was such that the residence time of the slurry in the sample train was small compared to that of the vessel from which the sample was drawn. A possible exception to this criteria was the marble bed itself. The liquid residence time in the marble bed is on

TABLE 5-7
TOTAL SULFUR MATERIAL BALANCE SUMMARY - CE PROTOTYPE TESTS 17R-20R

(All values in gmoles/min Total S)

Run	Set	Marble Bed In	Marble Bed Out	Hold Tank In	Hold Tank Out
17R	1	21.8	19.3	24.4	24.1*
	2	21.5	19.1	10.2	8.6
18R	1	119	135	137	142
	2	114	129	126	116
19R	1	66.8	70.95	58.2	60.5
	2	70.5	71.05	60.8	59.4
20R	1	57.35	59.0	47.4	51.0
	2	58.55	56.9	48.2	53.9

---

*17R, Set 1 hold tank samples taken independently of scrubber samples.

the order of 30 seconds while the sampling time is about 5-10 seconds.

Care was taken to obtain slurry samples from vertical lines where possible. This was done to avoid errors due to vertical gradients in slurry solids concentration. The severity of possible sampling errors due to radial gradients and non-isokinetic sampling was checked experimentally. The solids concentrations in samples drawn through a non-isokinetic side tap were compared to those obtained using an approximately isokinetic center probe. This was done in two- and three-inch vertical lines having markedly different slurry velocities and particle size distributions. The side tap produced results only 2-3% lower than the isokinetic center probe. The solids concentrations were measured by quantitative filtration and weighing of solids from a known weight of slurry.

Calculation of solid-liquid reaction rates for this system requires very accurate material balances. For this reason, it was essential to sample process streams around a given vessel in a proper and rapid sequence. The compositions of the downcomer and scrubber bottoms streams can vary considerably due to fluctuations in oxidation rate, SO_2 removal rate, and additive rate. These streams were sampled three times consecutively as they entered the hold tank over a period of about one residence time. The hold tank effluent itself was then sampled. This procedure results in an accurate time average of reactant concentration entering the tank. Rate calculations are thus not affected by short term fluctuations in stream compositions.

The composition of the scrubber spray should not change significantly during sampling around the marble bed.

Previous experiments showed that the marble bed itself is non-uniform, however. Two samples of the marble bed liquor were taken; one at the back and one at the front of the scrubber. These results were averaged for use in rate and material balance calculations. It was assumed that the marble bed samples were representative of streams leaving the scrubber through the downcomers.

The scrubber bottoms sample is probably the least representative of the actual process stream. This is due to sampling from a large short section of pipe that is not full or in turbulent flow. The contribution to the scrubber material balance from this stream is fortunately small.

Analytical methods used have been described in (Radian Final Report for EPA Contract CPA-70-143). Aqueous SO_2 analyses and percent solids determinations were completed on site. The remainder of the analyses was performed at Radian after shipping the samples to Austin. The pH measurements were made with a Beckman laboratory pH meter carefully standardized and temperature compensated. This instrument was located so that the slurry could be continuously directed from the pump into a beaker containing the electrodes. The error due to additive dissolution was kept at a minimum in this manner.

5.4.2 Precipitation and Dissolution Rates

The precipitation rates of $CaSO_3 \cdot \frac{1}{2}H_2O$, $CaSO_4 \cdot 2H_2O$, and $CaCO_3$, the dissolution rate of $Ca(OH)_2$, and the oxidation rate of SO_2 were calculated for the hold tank and the marble bed. Sample calculations of precipitation, dissolution, and oxidation rates are presented in Appendix E of this report. A summary of these precipitation, dissolution, and oxidation rates is presented here in Table 5-8.

TABLE 5-8

LIMESTONE INJECTION WET SCRUBBING TESTS - RATE CALCULATION SUMMARY

(All values in gmoles/min.)

	17R				18R		19R				20R				21R		22R	
	Solid Balance		Liquid Balance		Liquid Balance		Solid Balance		Liquid Balance		Solid Balance		Liquid Balance		Liquid Balance		Liquid Balance	
	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2
Marble Bed																		
SO_2 Oxidation	3.8	4.2	3.5	3.3	3.4	3.4	-.4	-.7	3.4	3.4	.9	1.8	3.7	3.7	3.7	3.7	4.5	4.5
$CaSO_3$ Precipitation	1.3	.8	1.6	1.75	5.7	4.6	1.6	1.0	-3.0	2.6	1.2	.3	-.7	-1.5	2.5	-.45	4.0	4.5
$CaSO_4$ Precipitation	-.8	-.4	1.0	.7	1.2	.4	-.6	-1.8	-.7	.8	-1.1	2.6	.8	1.9	2.0	1.65	.3	.2
$CaCO_3$ Precipitation	.5	0	**	**	**	**	-.8	.4	**	**	-.6	.7	**	**	**	**	**	**
$Ca(OH)_2$ Dissolution	5.2	3.3	6.9	5.3	7.7	6.9	4.5	3.4	1.6	9.4	4.8	5.9	5.5	4.1	9.1	4.9	7.8	8.7
SO_2 Removal	7.8	7.6	7.8	7.6	12.1	12.1	7.5	7.5	7.5	7.5	6.75	6.75	6.75	6.75	10.2	10.2	13.0	13.0
System Additive Rate	10.9	10.9	10.9	10.9	10.9	10.9	14.8	14.8	14.8	14.8	14.8	14.8	14.8	14.8	15.7	15.7	15.7	15.7
Hold Tank	*																	
SO_2 Oxidation	-.2	.7	**	**	**	**	-.3	-.2	**	**	-.6	.1	**	**	**	**	**	**
$CaSO_3$ Precipitation	7.2	1.5	7.0	2.3	1.8	2.4	6.0	5.2	5.5	5.0	4.1	2.8	2.7	2.7	1.3	3.9	12.4	8.3
$CaSO_4$ Precipitation	1.1	-.1	1.7	.7	.6	1.3	2.3	1.4	0	.6	1.2	1.6	-1.1	-1.9	-.1	3.4	8.4	2.9
$CaCO_3$ Precipitation	1.0	.5	.5	.2			.2	0	**	**	.1	.2	**	**	**	**	**	**
$Ca(OH)_2$	5.0	2.0	5.0	1.6	3.4	3.7	5.2	4.4	7.8	3.3	3.3	4.7	.6	.9	-3.8	5.0	12.4	5.5
SO_2 Removal	?	7.6		7.6	12.1	12.1	6.2	6.2	6.2	6.2	8.0	8.0	8.0	8.0	10.2	10.2	13 0	13 0
System Additive Rate	?	10.9		10.9	10.9	10.9	14.8	14.8	14.8	14.8	14.8	14.8	14.8	14.8	15.7	15.7	15.7	15.7
Total Rates																		
SO_2 Oxidation		4.9	3.5	3.3	3.4	3.4	-.9	-.9	3.4	3.4	0.3	1.9	3.7	3.7	3.7	3.7	4.5	4.5
$CaSO_3$ Precipitation		2.3	8.6	4.1	7.5	7.0	7.6	6.2	2.5	7.6	5.3	3.1	2.0	1.2	3.8	3.5	16.4	12.8
$CaSO_4$ Precipitation		-0.5	2.7	1.4	1.8	1.7	1.7	0.4	-0.7	1.4	0.1	4.2	-0.3	0.0	1.9	5.3	6.7	3.1
$CaCO_3$ Precipitation		0.5	0.5	0.2			-0.6	0.4			-0.5	0.9						
$CaOH_2$ Dissolution		5.3	11.9	6.9	11.1	10.6	9.7	9.8	9.4	12.7	8.1	10.6	6.1	5.0	5.3	9.9	20.2	14.2

---

*In Run 17 Set 1, Hold Tank rates were measured under different operating conditions than the scrubber rates.

**These rates were assumed to be negligible.

Two methods for checking the plausibility of these rates are:

(1) the sum of $Ca(OH)_2$ dissolution in the hold tank and the scrubber should not exceed the additive rate,

(2) the sum of $CaSO_3$ and $CaSO_4$ precipitation rates in the hold tank and the scrubber should not exceed the SO_2 removal rate.

The most consistent rate data presented in Table 5-8 are enclosed by brackets. In general the marble bed rates were less reasonable than the hold tank rates. This can be attributed to the instability of the marble bed and to marble bed sampling problems. However, for each limestone injection test, at least one good set of rates was obtained.

One objective of the limestone injection/wet scrubbing test series was to confirm the precipitation rate correlations derived through laboratory research on precipitation kinetics (Section 4.0 of this report). The observed precipitation rate correlations can be expressed by an equation of the form:

$$R = kn(r-1) \tag{5-4}$$

where R is the precipitation rate in g-moles/gram-min., k is the precipitation rate constant (g-mole/min-active site), n is the number of active sites for precipitation per gram of seed, and r is the relative saturation of the precipitating species. This is equal to the activity product of precipitating ions divided by the solubility product.

To compare the precipitation rates observed in the limestone injection/wet scrubbing tests with the precipitation rates observed in Radian laboratory studies, the hold tank precipitation rates enclosed by brackets in Table 5-8 were adjusted to the same temperature (45°C) using the Arrhenius rate constant equation with an activation energy of 15 kcal/g-mole. The amount of seed crystals in the slurry was calculated from the slurry analyses. The total amount of seed in the hold tank could then be calculated using the volume of the tank. Results of these calculations are presented in Table 5-9.

The relative saturations of the precipitating species were calculated using an equilibrium computer program and are also presented in Table 5-9.

Using the data presented in Table 5-9, plots were made of the precipitation rates in millimole/gram minute (at 45°C) versus relative saturation. These plots are shown in Figure 5-5 for $CaSO_3$ precipitation in the hold tank and in Figure 5-6 for $CaSO_4$ precipitation in the hold tank. Precipitation rates for the marble bed were not correlated due to rate errors resulting from marble bed sampling problems.

Referring to Figure 5-5, the sulfite precipitation rates calculated from hold tank balances are in general agreement with Equation 5-4. The data are quite scattered, however. A curve representing laboratory rate data for sulfite precipitation at 45°C is also shown in Figure 5-5. With the exception of Run 17, the pilot data lie far below this curve. Apparently, the crystals circulating in the pilot unit were less reactive than those used in the laboratory study.

Figure 5-6 shows sulfate precipitation rates for the injection scrubbing tests. These data agree quite well with

TABLE 5-9

HOLD TANK PRECIPITATION RATE CORRELATION INJECTION-WET SCRUBBING TESTS

Run	Set	Calculated Rate (gmoles/min)		Hold Tank Volume (gal)	Relative Supersaturation		Temp °C	Slurry Seed Concentration (g/liter)		Normalized Rate (mmoles/min-gram seed)	
		$CaSO_3$	$CaSO_4$		$CaSO_3$	$CaSO_4$		$CaSO_3$	$CaSO_4$	$CaSO_3$	$CaSO_4$
17R	1*	7.0	1.7	6000	2.8	1.13	51	1.91	0.71	0.090	0.048
	2	2.3	0.7	6000	4.6	0.5	37.5	0.60	0.10	0.277	
18R	1	1.8	0.6	6000	2.7	1.16	46	5.24	10.99	0.014	0.002
	2	2.4	1.3	6000	4.4	1.18	46	4.26	8.3	0.024	0.007
19R	1	5.5	2.3	6000	9.9	1.28	39	2.94	1.62	0.144	0.057
	2	5.0	1.4	6000	11.4	1.24	39	2.84	1.52	0.145	0.052
20R	1	4.1	1.2	6000	7.8	1.39	40	1.41	0.81	0.212	0.106
	2	2.8	1.6	6000	10.4	1.51	40	1.11	0.70	0.179	0.167
21R	1	1.3	-0.1	3000	3.0	1.25	45	25.55	18.48	0.009	
	2	3.9	3.4	3000	3.8	1.17	45	21.43	10.50		0.014
22R	1	12.4	8.4	6000	4.0	0.96	46	28.44	19.69	0.017	
	2	8.3	2.9	6000	3.7	1.11	45				

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*These data were taken before the use of blowdown and are not comparable to other data in the table.

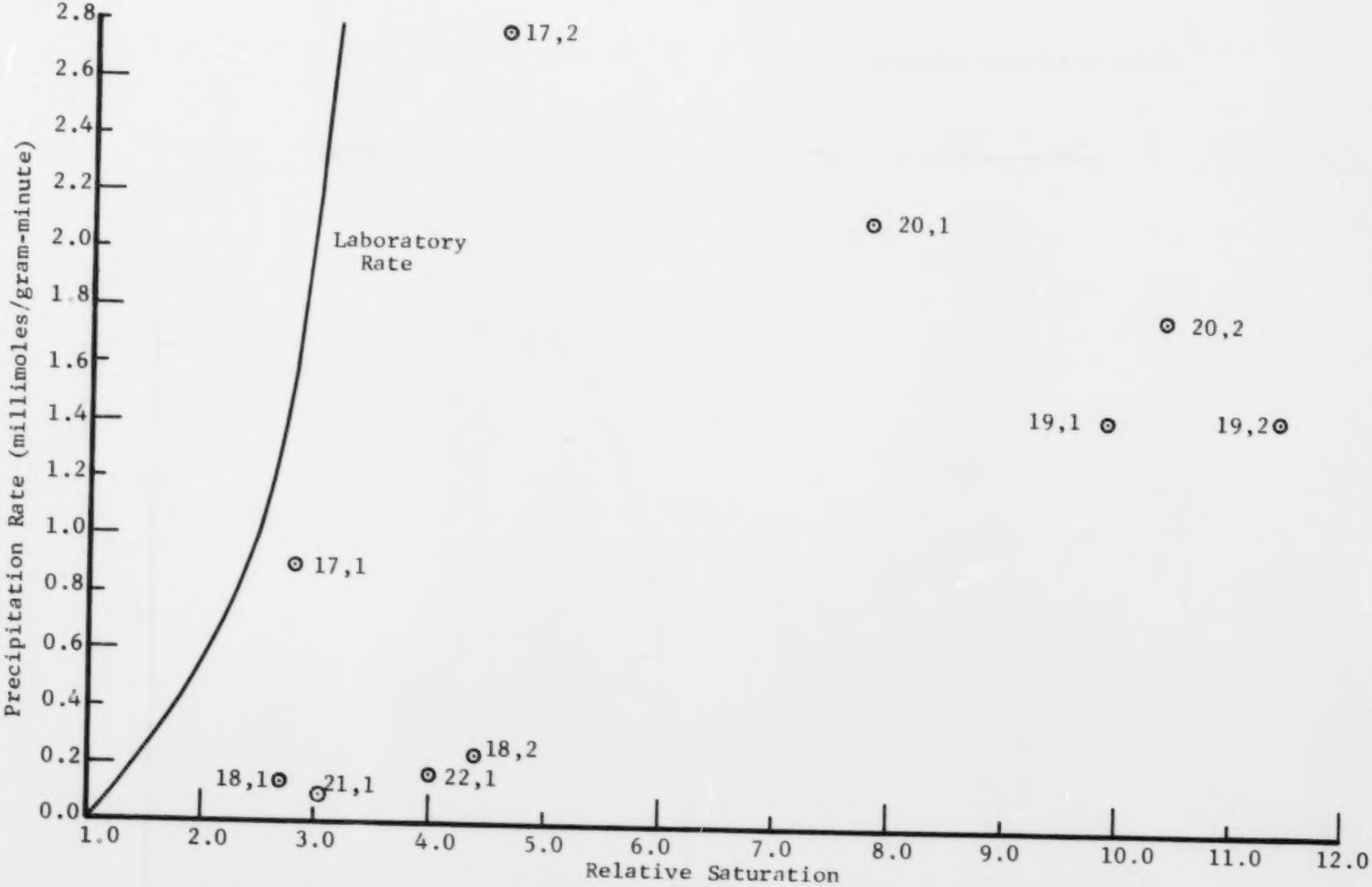

FIGURE 5-5 - $CaSO_3$ PRECIPITATION RATE IN HOLD TANKS FOR LIMESTONE INJECTION TESTS

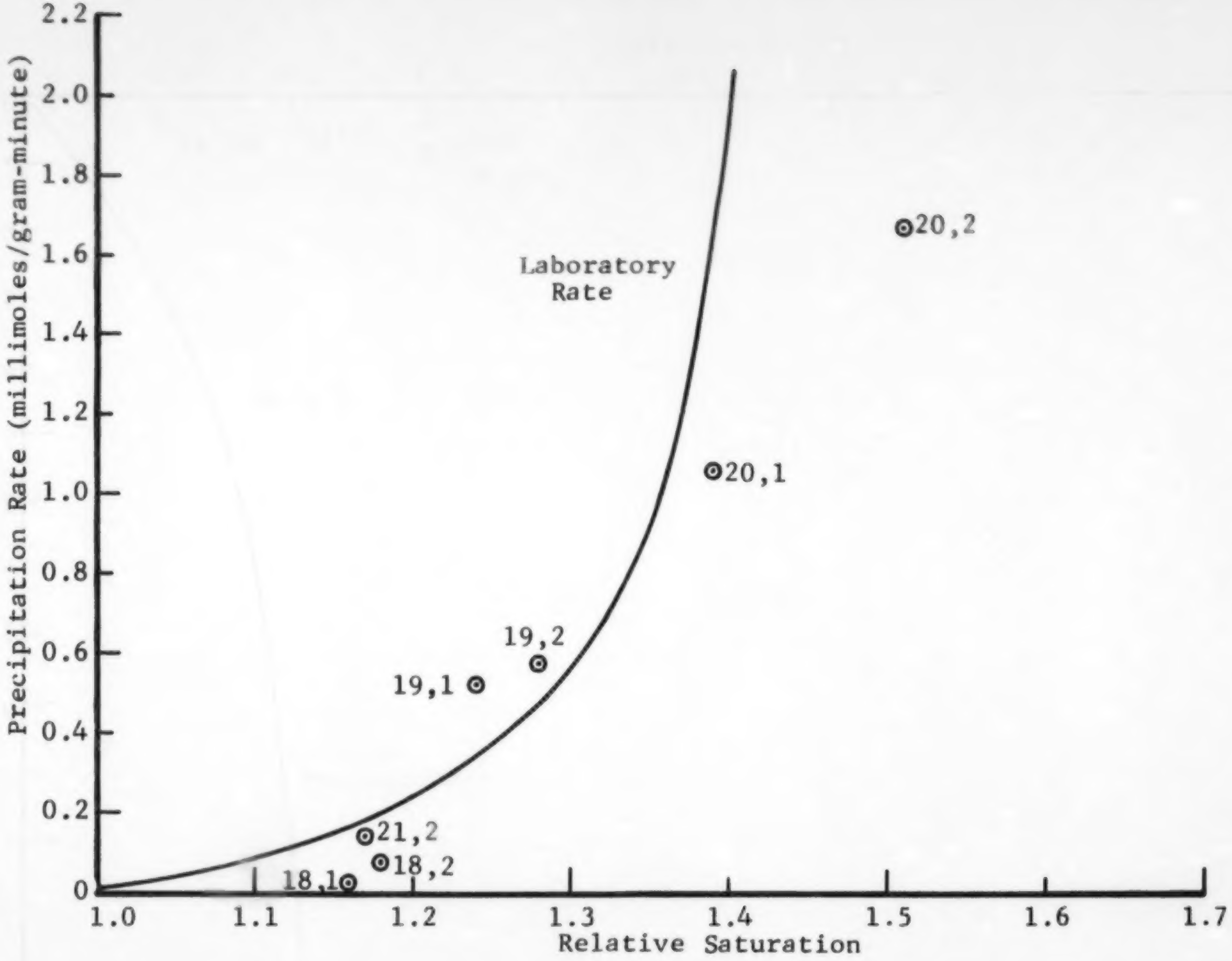

FIGURE 5-6 - $CaSO_4$ PRECIPITATION RATE IN HOLD TANKS FOR LIMESTONE INJECTION TESTS

Equation 5-4. They are also in good agreement with laboratory results.

5.4.3 Vapor-Liquid Mass Transfer Rates

In the same manner as the soluble tests, vapor-liquid equilibrium calculations were made for the marble bed scrubber in each limestone injection/wet scrubbing tests. Relative mass transfer coefficients were again calculated using Test 9R as a reference point.

The data given in Tables 5-10 and 5-11 indicate that the mass transfer capability of the marble bed scrubber is strongly dependent on the liquor pH in the same manner as in the soluble sodium carbonate test series. This trend is exhibited in Figure 5-7 which plots $K_g a$ vs. pH for both the soluble sodium carbonate tests and for the limestone injection tests.

The operating variables of flue gas flow rate, liquid to gas ratio, flue gas temperature, and liquor flow rate do not appear to have as significant an effect on relative mass transfer as do percent solids in the scrubber spray. This effect of the percent solids in the scrubber spray is probably due to its effect on the scrubber operating pH through dissolution of lime in the bed.

5.4.4 Prediction of Scaling Conditions

Another objective of these tests was to determine the ability to predict scaling conditions in the scrubber based upon calculated supersaturations. Laboratory studies have related scaling to rapid nucleation of calcium sulfite and calcium

TABLE 5-10
MARBLE BED VAPOR-LIQUID EQUILIBRIUM CALCULATIONS

Run	pH Range	$y^*_{SO_2}$ (ppm)	$y^*_{CO_2}$ (atm)
17R	4.5-5.5	10-50	.05-.06
18R	5.8-6.2	0	.07-.18
19R	4.5-4.9	10-35	.03
20R	4.5-4.7	10-20	.025
21R	5.4-5.7	0	.025-.03
22R	5.4-6.1	0	.01-.025

TABLE 5-11
RELATIVE MASS TRANSFER COEFFICIENTS

(Based on K_ga for Experiment 9R of the soluble test series set equal to 1.0)

Experiment	Liquor pH	y_{SO_2} (ppm) Inlet	y_{SO_2} (ppm) Outlet	$y^*_{SO_2}$ (ppm)	N.T.U. $= \ln \frac{y_{in}-y^*}{y_{out}-y^*}$	Relative K_ga
17R	4.5-5.5	1,500	750	50	.7	.7
18R	5.8-6.2	1,500	390	0	1.35	1.35
19R	4.5-4.9	1,880	1,060	35	.6	.55
20R	4.5-4.7	1,950	1,250	20	.45	.4
21R	5.4-5.7	2,000	810	0	.9	.8
22R	5.4-6.1	2,020	555	0	1.3	1.2

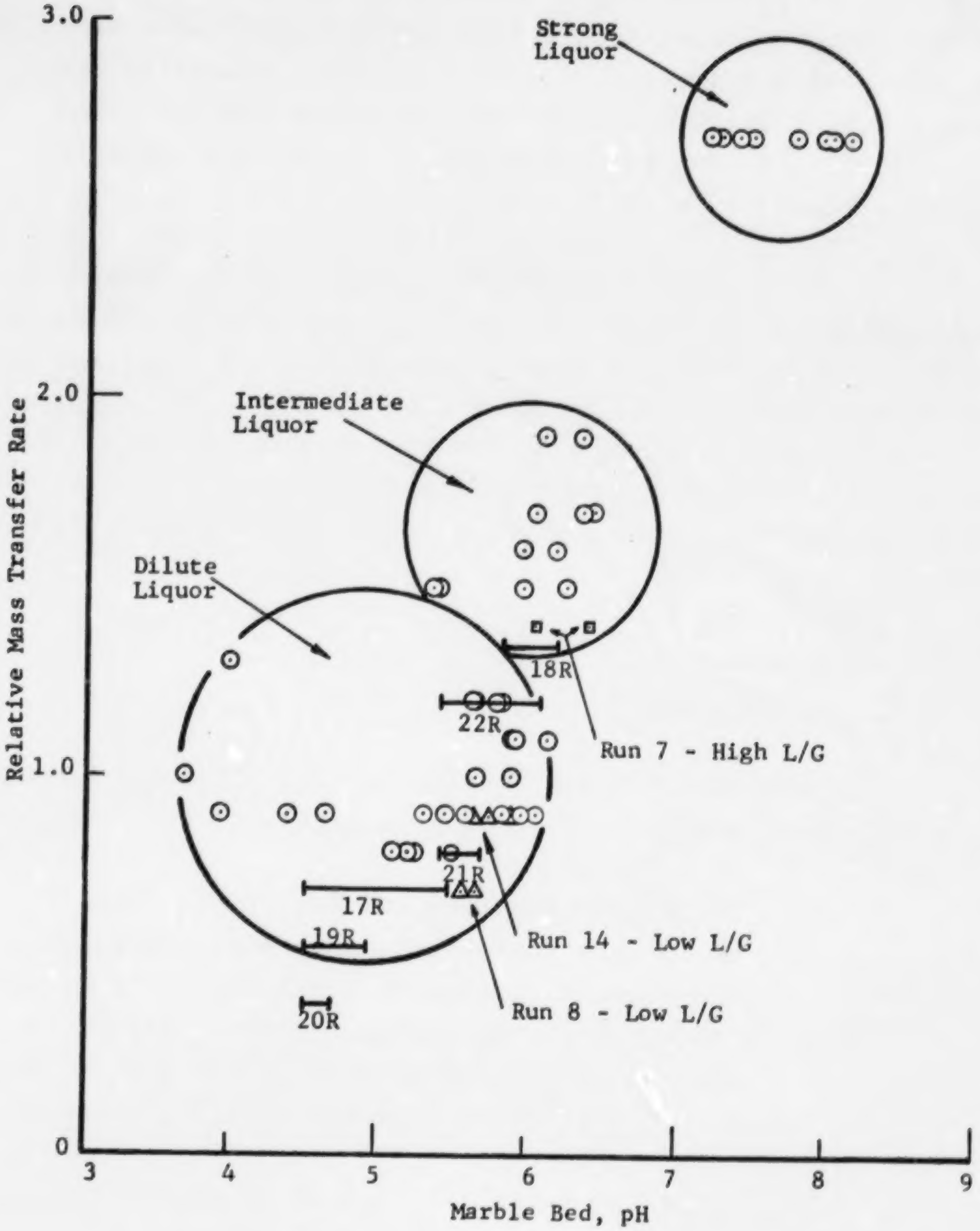

FIGURE 5-7 - RELATIVE MASS TRANSFER RATE VS. pH FOR SOLUBLE TEST AND LIMESTONE INJECTION TESTS

sulfate at supersaturations exceeding the "metastable limit". Experimentally determined values for the metastable limit of calcium sulfate are 1.3 - 1.4 and of calcium sulfite are 3.0 - 4.0. Observations of scaling during the limestone injection/wet scrubbing tests are compared with predicted scaling behavior in Table 5-12.

In general the results are excellent. Taking into consideration the possible errors in measurements and calculations, the sulfate metastable limit of 1.3 - 1.4 appears to be an adequate criterion for predicting scaling. The sulfite limit of 3 - 4, on the other hand, may be somewhat conservative. No sulfite scale was observed in Test 21R where the marble bed sulfite supersaturation ranged as high as 6.8 and in Test 22R where 5.0 was reached.

5.4.5 Conclusions

From the results obtained in the limestone injection/wet scrubbing tests the following conclusions were drawn.

(1) The slurry sampling and analytical techniques applied in these tests adequately revealed the chemical processes occurring in limestone injection/wet scrubbing systems. Difficulty was encountered in characterizing the marble bed due to its non-uniform composition, however.

(2) Operating variables such as additive rate, flue gas flow rate, liquid to gas ratio, and liquor flow rate appear to affect the overall vapor-liquid mass transfer rate only through their

TABLE 5-12

PREDICTION OF SCALING USING CALCULATED RELATIVE SUPERSATURATIONS

Run	Sulfite Supersaturation	Sulfate Supersaturation	Predicted Scaling	Observed Scaling
17R	2.1-5.2	.85-1.08	Possible sulfite. No sulfate.	Minor scaling. Composition not reported.
18R	4.8-11.4	1.16-1.28	Definite sulfite. Possible sulfate.	Scale observed: 55-65% sulfite 25-45% sulfate
19R	3.1-7.4	1.8-2.6	Possible sulfite. Definite sulfate.	Scale observed, sulfate (preliminary analysis).
20R	1.7-2.9	2.0-2.2	No sulfite.	Scale observed, sulfate (preliminary analysis).
21R	3.9-6.8	1.2-1.6	Possible sulfite. Possible sulfate.	No scale observed.
22R	3.4-5.0	1.2-1.4	Possible sulfite. Possible sulfate.	No scale observed.

effect on the operating pH of the marble bed. This correlation between vapor-liquid mass transfer and pH indicates that a liquid phase resistance is a significant portion of the overall vapor-liquid mass transfer rate.

(3) The precipitation rates observed in the limestone injection/wet scrubbing tests could be described by the same general form as the rate correlation observed in Radian laboratory research.

$$R = kn(r-1) \tag{5-4}$$

Therefore, circulation of large amounts of solids in the slurry increases the precipitation of and decreases the supersaturation of $CaSO_3$ and $CaSO_4$ in the scrubbing system. The magnitude of sulfite precipitation rates was considerably lower in the pilot unit than in the laboratory study, however. Sulfate precipitation rates were comparable.

(4) Over half of the system additive dissolution occurs in the scrubber in spite of low liquid residence times. The additive dissolution rate is apparently a strong function of liquor pH.

(5) Safe supersaturation limits for scale-free operation agree with those established in the laboratory for calcium sulfate (1.3-1.4), but appear to be higher for calcium sulfite. The limestone injection/wet scrubbing system operated in a scale-free condition with calcium sulfite supersaturation levels up to 6-8.

5.5 Limestone Tail-End Addition Tests

This portion of the final report outlines the results and conclusions obtained by Radian Corporation from the Phase III limestone tail-end addition/wet scrubbing tests. The objectives of these tests were presented in Section 5.3.1 of this report. The flow scheme and operating conditions of these tests were presented in Figures 5-3a and 5-3b, and in Table 5-3 of this report.

5.5.1 Analytical Results

The results from Radian laboratory analysis of the liquid and solid phases of the slurry samples taken in the limestone tail-end addition/wet scrubbing tests are presented in Appendix D of this report. Electroneutrality imbalances were determined for each of the liquid phase chemical analyses. For the slurry sample analysis from the limestone tail-end addition tests the electroneutrality imbalances were below 4% except for Test 3A where four of the slurry sample analyses had electroneutrality imbalances of 5% - 7%. Errors up to 5% are to be expected in the chemical analysis of slurries of this nature.

Total sulfur material balances were performed around the marble bed scrubber and the hold tank as a check on the accuracy of both the sampling techniques and the analytical techniques employed. The results of these material balance calculations are presented in Table 5-13.

TABLE 5-13

TOTAL SULFUR MATERIAL BALANCE SUMMARY CE LIMESTONE TESTS

(All values in gmoles/min total S)

		Marble Beds			Hold Tank		
Run	Set	In	Out	Deviation from Mean (%)	In	Out	Deviation from Mean (%)
1A	1	193	212	9.4	185	191	3.1
	2	202	233	14.3	192	187	2.6
2A	1	-	-	-	-	-	-
	2	292	275	5.6	312	299	4.3
3A	1	375	386	2.9	365	367	0.5
	2	-	-	-	367	338	8.2
1B	1	359	429	17.7	363	354	2.5
	2	406	420	3.4	381	376	1.3
2B	1	809	953	16.3	720	968	20.4
	2	919	1,124	20.1	827	865	4.5
3B	1	-	-	-	-	-	-
	2	-	-	-	-	-	-

Excluding Test 2B the average deviation in the sulfur material balances was 10% for the marble bed and 4% for the hold tank. The 29% material balance deviation for the hold tank in Test 2B was probably due to an error in the weight percent solids determination. The marble bed sulfur material balances consistently have greater deviations due to problems in obtaining slurry samples representative of the marble bed.

It should be noted here that for slurries with high solids content, the total sulfur material balance is not a good indication of the accuracy of the liquid phase analyses since most of the sulfur is in the solid phase.

5.5.2 Precipitation and Dissolution Rates

As in the injection/scrubbing test series, the precipitation rates of $CaSO_3$ were calculated for the hold tank and for the marble bed. These rate calculations were performed using the chemical analyses of the slurry samples taken during the limestone tail-end addition tests sample calculations of these rates are given in Appendix E of this report. The results of these calculations are summarized in Table 5-14.

No attempt was made to perform separate material balances or rate calculations around the lower and upper marble beds during the double bed runs. Possible transfer of liquor between beds and lack of an intermediate gas sampling point precluded this calculation.

Of the rates presented in Table 5-14, the marble bed rates contained the largest errors. These errors were due to

TABLE 5-14

RATE CALCULATION SUMMARY FOR LIMESTONE TAIL-END ADDITION TESTS

Liquid Balances (mmoles/min)

	Run 1A		Run 2A		Run 3A		Run 1B		Run 2B		Run 3B	
	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2
Marble Beds												
SO_2 Oxidation	2,540	2,540	3,400	3,400	2,930	---	4,250	4,350	5,940	5,870	5,750	5,990
$CaSO_3$ Precipitation	-3,160	-270	-2,990	-3,150	210	---	520	90	2,710	3,010	-3,600	-5,330
$CaSO_4$ Precipitation	2,690	260	2,510	1,900	4,870	---	1,030	1,440	-790	-380	40	890
$CaCO_3$ Dissolution	4,360	5,690	7,460	5,530	6,010	---	8,130	9,690	12,360	12,020	9,420	8,900
Hold Tank												
SO_2 Oxidation	*	*	*	*	*	*	*	*	*	*	*	*
$CaSO_3$ Precipitation	3,980	-1,890	7,390	8,910	10,250	9,000	8,330	7,860	8,140	9,890	12,080	14,590
$CaSO_4$ Precipitation	920	4,580	560	580	-2,710	-570	1,270	1,520	4,000	2,430	3,510	3,870
$CaCO_3$ Dissolution	2,350	3,360	3,765	4,773	3,810	4,780	5,310	4,720	5,690	5,940	6,580	9,060
Surge Tanks												
SO_2 Oxidation	*	*	*	*	*	*	*	*	*	*	*	*
$CaSO_3$ Precipitation	7,386	4,364	6,104	5,357	500	---	4,410	4,740	3,460	1,800	4,380	4,990
$CaSO_4$ Precipitation	-1,620	863	976	1,430	2,840	---	2,160	1,778	2,910	3,970	2,630	550
$CaCO_3$ Dissolution	3,744	2,028	1,836	3,042	620	---	2,270	2,800	2,080	2,220	2,248	2,230
SO_2 Removal Rate	10,600	10,600	11,600	11,600	12,200	12,200	17,000	17,400	21,200	20,980	19,160	19,950
System Additive Rate	34,440	34,440	35,336	35,336	21,440	21,440	36,940	36,940	36,940	36,940	22,910	22,910
Total S Precipitation	10,200	7,910	14,550	15,030	15,960	---	17,700	17,400	20,400	20,700	19,000	19,600
Total $CaCO_3$ Dissolution	10,450	11,080	13,060	13,350	10,440	---	15,700	17,200	20,100	20,200	18,200	20,200
Total S Removed from Flue Gas	10,600	10,600	11,600	11,600	12,200	---	17,000	17,400	21,200	21,000	19,200	20,000
Total SO_2 Oxidation	2,540	2,540	3,400	3,400	2,930	---	4,250	4,350	5,940	5,870	5,750	5,990
Total $CaSO_4$ Precipitation	1,990	5,703	4,050	3,910	5,000	---	4,460	4,740	6,120	6,020	6,180	5,310

sampling probe and sampling line problems which limited ability to collect representative slurry samples.

The $CaSO_4 \cdot 2H_2O$ precipitation rate in the hold tank for Test 3A is negative indicating dissolution of $CaSO_4 \cdot 2H_2O$. This is also substantiated by sub-saturation levels of $CaSO_4$ in the hold tank. Since Test 3A was the first test in the series, this condition may indicate that steady state operation had not been reached.

Because the rate calculations around the hold tank and the marble bed did not appear to account for all of the precipitation and dissolution occurring in the system, rate calculations were performed around the surge tanks. The results of the surge tank rate calculations are included in the rate calculation summary presented in Table 5-14. Agreement of the precipitation, dissolution, and SO_2 removal rates presented in Table 5-14 is good and indicates good overall accuracy for the results.

The precipitation rates observed in the limestone tail-end addition tests were compared with those observed in previous tests. Rates were again normalized to the common temperature of 45°C using the Arrhenius rate constant equation with an activation energy of 15 kcal/g-mole.

The normalized precipitation rates, the seed crystal density, and the relative supersaturations for both $CaSO_3$ and $CaSO_4$ are presented in Table 5-15. From the data presented in Table 5-15, plots were made of precipitation rates versus relative saturation for the data collected in the limestone tail-end addition tests. These plots are shown in Figure 5-8 for $CaSO_3$ precipitation in the hold tank and in Figure 5-9 for

TABLE 5-15

HOLD TANK PRECIPITATION RATE CORRELATION

TAIL-END ADDITION TESTS

Run	Set	Calculated Rate (gmoles/min) $CaSO_3$	Calculated Rate (gmoles/min) $CaSO_4$	Volume (gal)	Relative Supersaturation $CaSO_3$	Relative Supersaturation $CaSO_4$	Temp (°C)	Slurry Seed Concentration (g/liter) $CaSO_3$	Slurry Seed Concentration (g/liter) $CaSO_4$	Normalized Rate (mmoles/min-gram seed) $CaSO_3$	Normalized Rate (mmoles/min-gram seed) $CaSO_4$
1A	1	3.98	0.92	6,000	3.5	1.09	48.0	2.74	1.30	0.047	0.023
	2	-1.89	4.58	6,000	2.0	0.87	47.4	2.68	1.18	-0.024	0.132
2A	1	7.39	0.56	6,000	4.1	1.09	48.0	----	----	----	----
	2	8.91	0.58	6,000	4.8	1.12	47.0	2.77	1.15	0.114	0.018
3A	1	10.25	-2.71	6,000	8.4	0.80	49.0	3.50	1.55	0.086	-0.041
	2	9.00	-0.57	6,000	11.9	0.64	48.0	3.27	1.33	0.084	-0.013
1B	1	8.33	1.27	6,000	5.9	1.07	50.3	2.57	1.10	0.083	0.030
	2	7.86	1.52	6,000	1.6	1.12	50.8	2.68	1.25	0.072	0.030
2B	1	8.14	4.00	6,000	4.9	1.05	51.2	4.68	2.42	0.041	0.039
	2	9.89	2.43	6,000	4.2	1.05	50.4	4.13	2.18	0.061	0.029
3B	1	12.08	3.51	6,000	4.3	1.03	50.0	----	----	----	----
	2	14.59	3.87	6,000	4.2	1.03	50.0	----	----	----	----

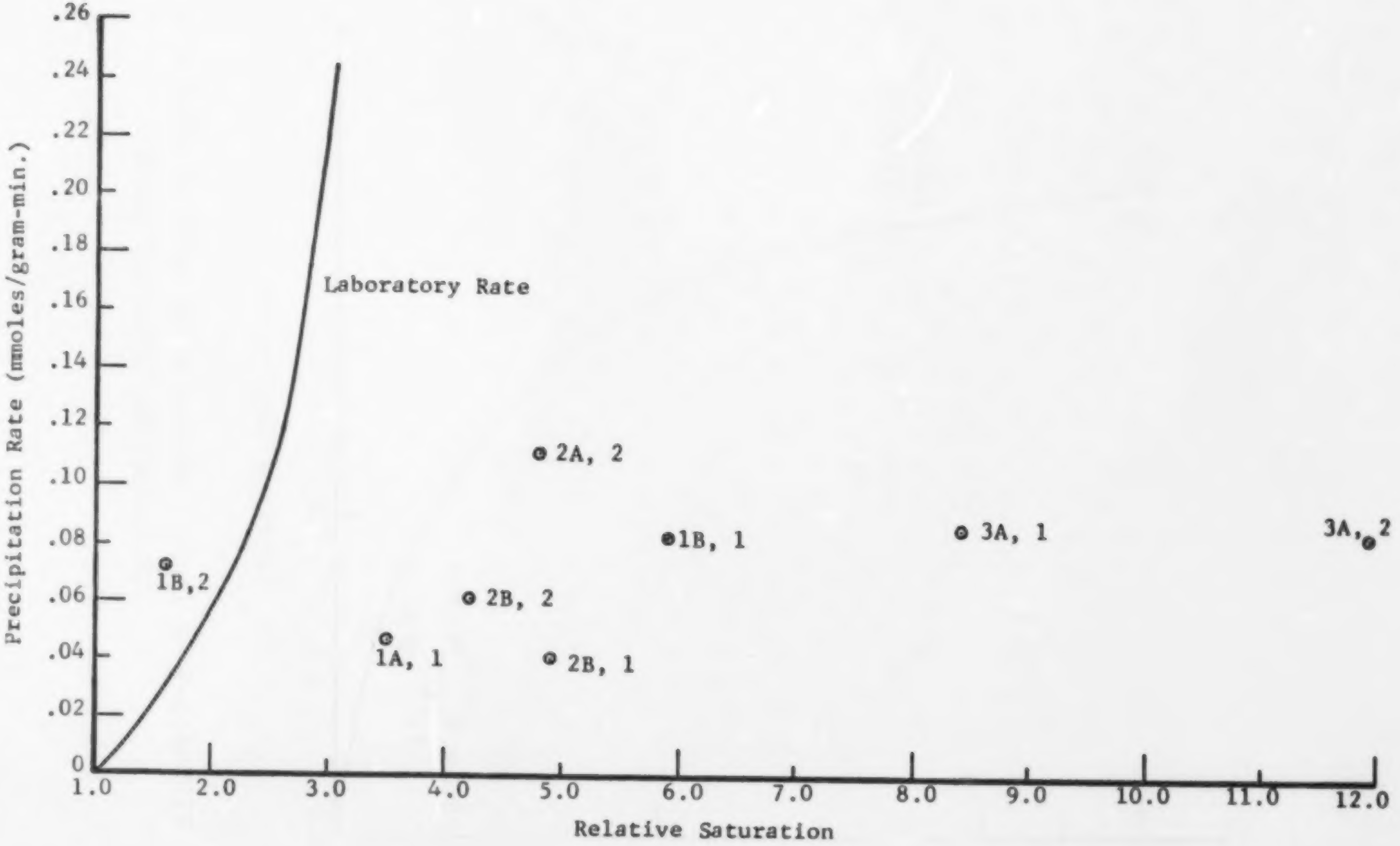

FIGURE 5-8 - $CaSO_3$ PRECIPITATION RATE IN HOLD TANK FOR LIMESTONE TAIL-END TESTS

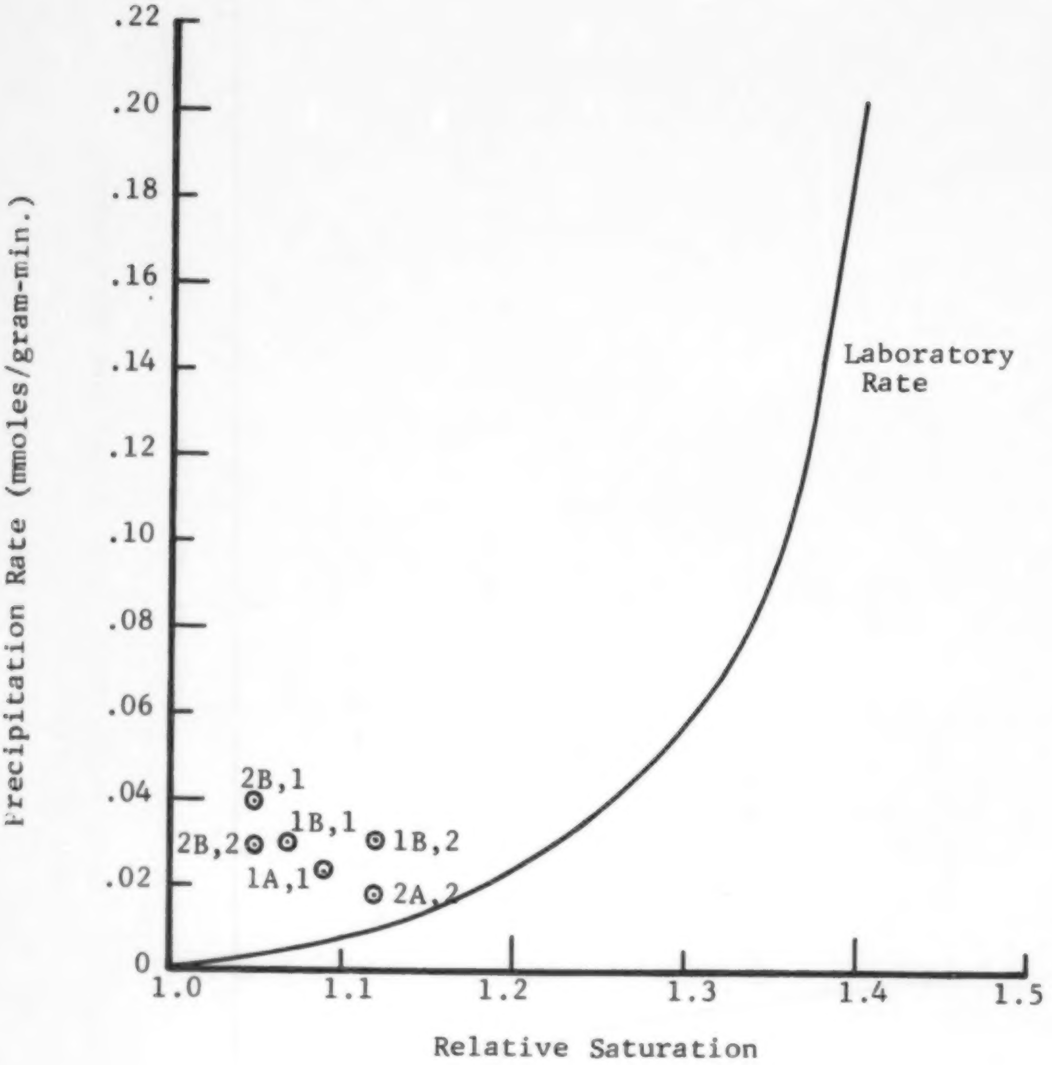

FIGURE 5-9 - $CaSO_4$ PRECIPITATION RATE IN HOLD TANK FOR LIMESTONE TAIL-END TESTS

$CaSO_4$ precipitation in the hold tank. Due to the unrealiability of the marble bed rate data, these precipitation kinetics comparisons were not made.

Figures 5-8 and 5-9 indicate that the precipitation rate data obtained from the limestone tail-end addition tests do not correlate well using the precipitation rate expression given by Equation 5-4. This scattering of data may be due to errors in the precipitation rates, or to the fact that the number of active sites for precipitation is only proportional to the mass of seed crystals when the crystal size distribution is constant for all tests.

Limestone dissolution rates measured in these pilot studies have been re-calculated on a per gram of limestone basis for comparison with laboratory results. Information pertinent to these calculations is summarized in Table 5-16. Figure 5-10 compares the laboratory and pilot scale results on a consistent basis. Considering the possibility of variations in particle size between the pilot scale and the laboratory tests, the agreement is excellent.

5.5.3 Vapor-Liquid Mass Transfer Rates

From the chemical analysis of the downcomer stream, vapor-liquid equilibrium calculations were again made for the marble bed scrubber in each limestone tail-end addition/wet scrubbing test. For the double bed runs the equilibrium SO_2 partial pressures for each bed were averaged due to the unavailability of data on the flue gas composition between the marble beds. The "relative K_ga" for the marble bed in each limestone tail-end addition test was calculated from the equilibrium SO_2 data presented in Table 5-17. These K_ga values are presented in Table 5-17 and are again relative to Test 9R.

TABLE 5-16

HOLD TANK LIMESTONE DISSOLUTION RATE CORRELATION

Run	Set	Limestone Dissolution Rate (moles/min)	Limestone Solids Concentration (wt %)	Density (g/ℓ)	Hold Tank Volume (liters)	a_{H^+} (10^{-7} mole/ℓ)	Limestone Dissolution Rate (mmole/gram min)
1A	1	2.4	3.2	1,080	22,700	8.9	.0031
	2	3.4	3.4	1,080	22,700	7.6	.0042
2A	1	3.8	**	**	22,700	10.0	**
	2	4.8	2.3	1,070	22,700	8.5	.0086
3A	1	3.8	2.5	1,080	22,700	8.9	.0062
	2	4.8	2.1	1,080	22,700	9.6	.0093
1B	1	5.3	2.3	1,070	22,700	4.9	+
	2	4.7	2.5	1,070	22,700	35.5	.0077
2B	1	5.7	2.9	1,110	22,700	9.1	.0078
	2	5.9	2.6	1,100	22,700	9.3	.0091
3B	1	6.6	**	**	22,700	12.3	**
	2	9.1	**	**	22,700	15.9	**

**wt % solid samples were lost for these runs.

+This value ignored because $a_{CO_3^=} > a^*_{CO_3^=}$.

TABLE 5-17

RELATIVE MASS TRANSFER COEFFICIENTS

(Based on K_ga for Experiment 9R of the soluble test series set equal to 1.0)

Experiment	Outlet Gas Flow Rate (gmoles/min)	Total Scrubber Liquid Rate (gpm)	Liquor pH	y_{SO_2} (ppm)		$y^*_{SO_2}$ (ppm)	NTU	Relative K_ga
				Inlet	Outlet			
1A	10,800	150	5.3-5.6	2,310	1,110	4.4	0.73	0.68
2A	10,600	240	5.0-5.2	2,505	1,010	7.8	0.91	0.83
3A	10,480	243	5.3	2,345	980	9.9	0.87	0.79
1B	10,700	310	5.6-6.0	2,410	545	1.1	1.49	1.37
2B	10,900	470	5.4-5.8	2,435	290	1.5	2.13	2.00
3B	10,800	485	5.0-5.6	2,375	365	5.2	1.87	1.74

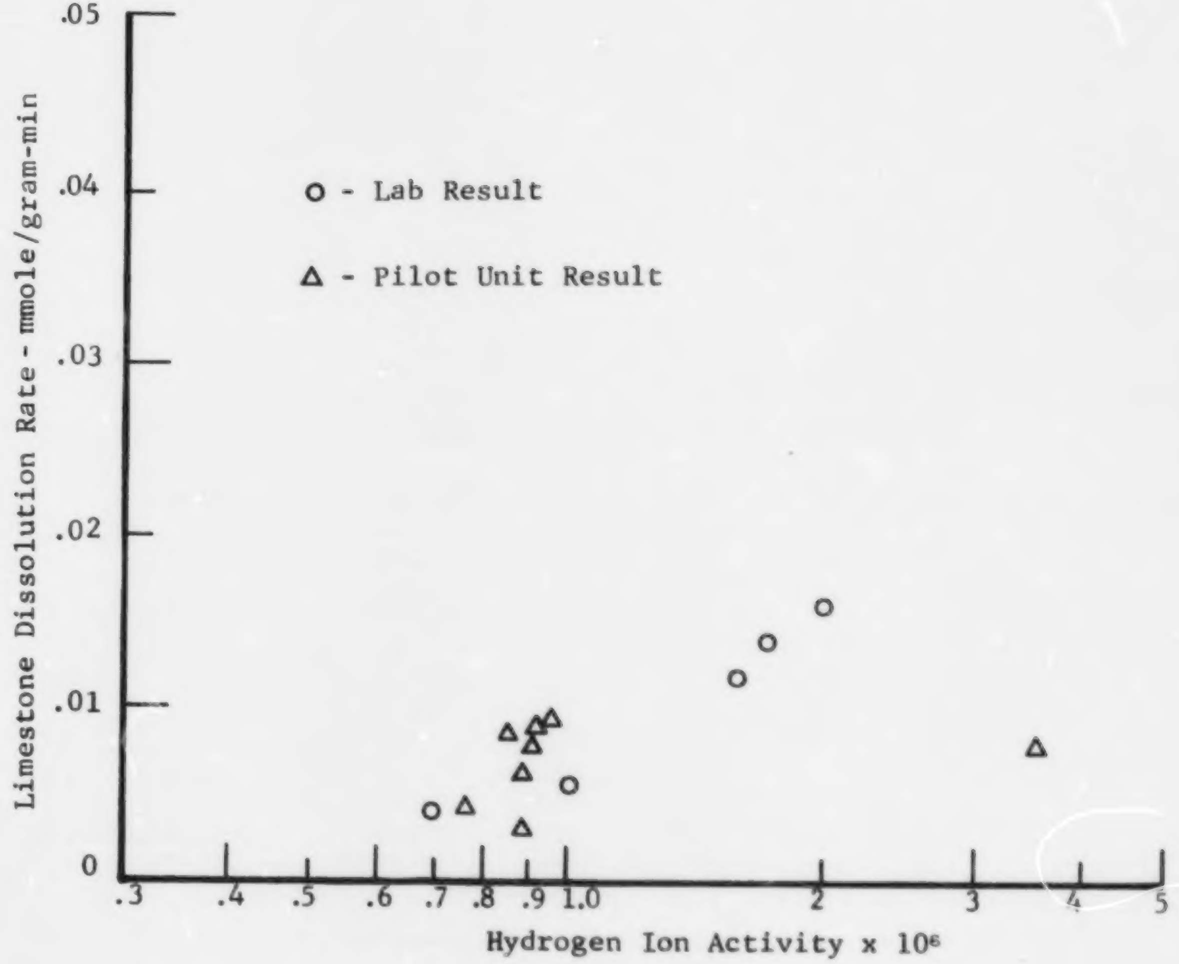

FIGURE 5-10 - COMPARISON OF LAB AND PILOT UNIT LIMESTONE DISSOLUTION RATES

In agreement with previous tests, there appears to be a proportional relationship between the relative mass transfer coefficient and the scrubber pH for the limestone tail-end addition experiments. This trend is exhibited in Figure 5-11 and indicates that the SO_2 removal is partially limited by a liquid-film diffusion rate.

Figure 5-11 also indicates that the limestone stoichiometry influences the overall mass transfer coefficient by its influence on the pH. The only difference in operating conditions between Tests 2A and 3A, and between Tests 2B and 3B is the limestone stoichiometry. In both cases the tests with the limestone stoichiometry of 96% had a lower $K_g a$ than the tests with the limestone stoichiometry of 145%. The limestone stoichiometry, by its influence on the limestone dissolution rate, may have an influence on the liquid film resistances and the liquid film diffusion rates.

5.5.4 Prediction of Scaling Conditions

Laboratory studies have shown that scaling is related to rapid nucleation of calcium sulfite and sulfate at supersaturations exceeding the so-called "metastable limit". Predicted scaling behavior for the tail-end addition tests based on the metastable limits of 3.0 - 4.0 for $CaSO_3 \cdot \frac{1}{2}H_2O$ and of 1.3 - 1.4 for $CaSO_4 \cdot 2H_2O$ is presented in Table 5-18. Regardless of the several high supersaturations, there was no scaling observed during any of the limestone tail-end addition tests. No explanation is available for this phenomenon.

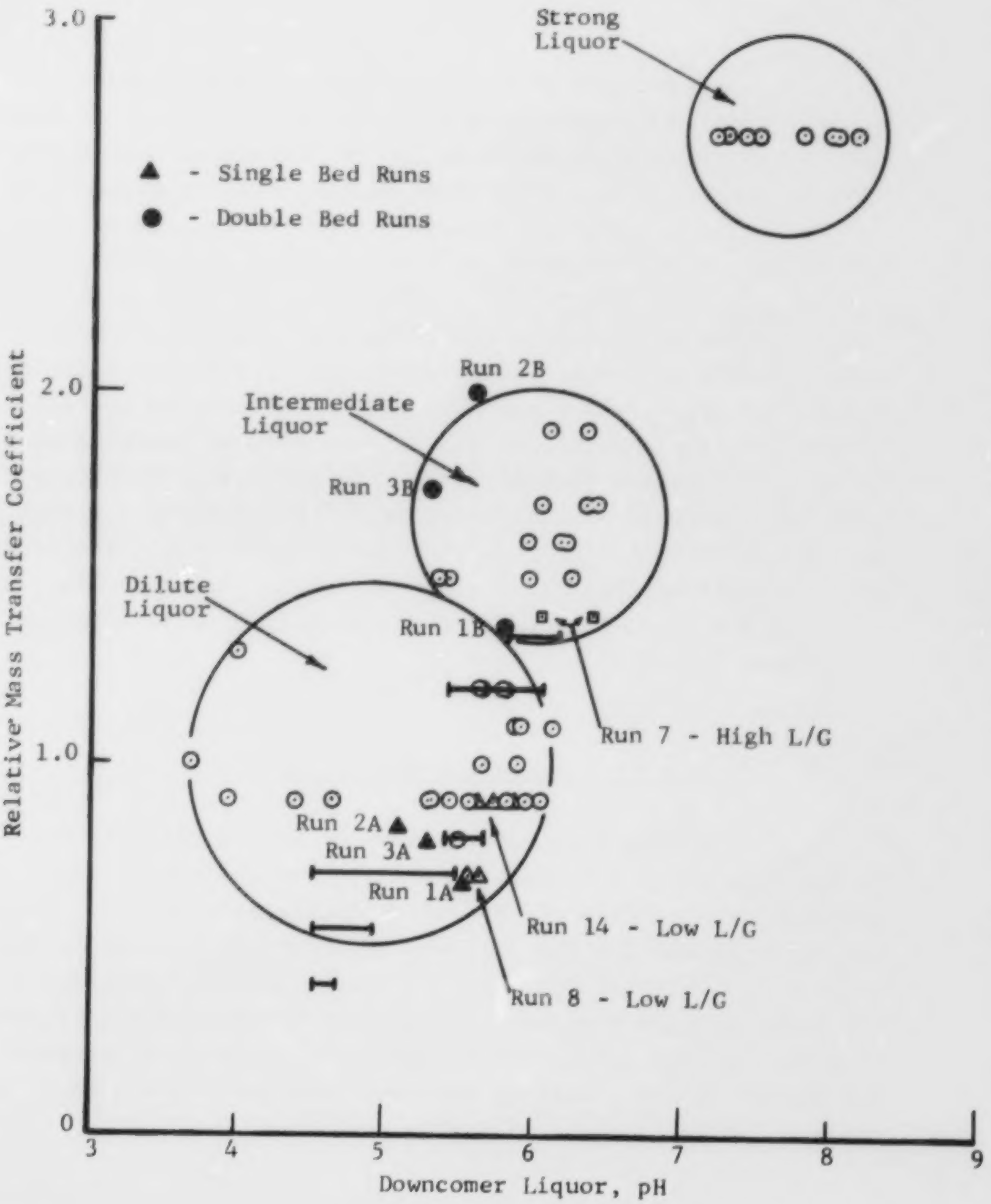

FIGURE 5-11 - RELATIVE MASS TRANSFER COEFFICIENT VS. pH

TABLE 5-18

PREDICTION OF SCALING USING CALCULATED RELATIVE SUPERSATURATIONS

Run	Vessel	Set	pH	Temperature (°C)	$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	Predicted Scaling
1A	Marble Bed	1	5.28	47.4	10.6	1.22	Definite Sulfite, Possible Sulfate
		2	5.59	47.2	14.0	1.41	
2A	Marble Bed	1	4.97	48.0	5.9	1.45	Possible Sulfite, Possible Sulfate
		2	5.19	46.0	8.6	1.57	
3A	Marble Bed	1	5.29	49.0	9.6	0.87	Definite Sulfite, No Sulfate
1B	Upper Marble Bed	1	5.76	46.6	11.6	1.43	Definite Sulfite, Possible Sulfate
		2	5.95	47.5	14.2	1.45	
	Lower Marble Bed	1	5.64	47.1	13.6	1.40	Definite Sulfite, Possible Sulfate
		2	5.90	47.5	17.9	1.28	
2B	Upper Marble Bed	1	5.81	45.5	6.0	1.40	Possible Sulfite, Possible Sulfate
		2	5.68	46.0	5.5	1.39	
	Lower Marble Bed	1	5.38	47.3	6.6	1.42	Possible Sulfite, Possible Sulfate
		2	5.52	44.4	7.9	1.38	
3B	Upper Marble Bed	1	5.60	47.0	5.8	1.38	Possible Sulfite, Possible Sulfate
		2	5.49	47.0	5.9	1.35	
	Lower Marble Bed	1	5.30	46.2	8.2	1.40	Possible Sulfite, Possible Sulfate
		2	5.05	48.9	5.2	1.33	

5.5.5 Conclusions

The data and calculations obtained for the six limestone tail-end addition/wet scrubbing tests support the following conclusions.

(1) The analytical and hold tank sampling methods employed were adequate for investigating important vapor-liquid and solid-liquid reaction rates in the process vessels. Poor results caused by marble bed sampling probe problems indicate the importance of very short sampling times.

(2) The amount of $CaSO_4 \cdot 2H_2O$ precipitation in the scrubber is always a substantial fraction of the total $CaSO_4 \cdot 2H_2O$ precipitation for the system (≈ 50%) in spite of the low liquid residence time in the marble bed. This is presumably due to high supersaturations and high nucleation rates in the marble beds. $CaSO_3 \cdot \frac{1}{2}H_2O$ precipitation in the marble bed is low, but significant (≈ 10%).

(3) Over 50% of the $CaCO_3$ dissolution in the wet scrubbing system occurs in the scrubber in spite of its relatively small liquid hold up. This is due to the high driving force for dissolution occurring in the marble beds. This is consistent with laboratory results showing a strong relationship between limestone dissolution rate and pH. Limestone dissolution rates in the hold tank agree well with laboratory results.

(4) Significant amounts of precipitation and dissolution occurred in the surge tanks. This reaction should be taken into account in pilot plant studies and process design.

(5) Vapor-liquid mass transfer rates were similar to those experienced in the lime and Na_2CO_3 test series. Their correlation with marble bed pH was again significant. It was also evident that there is a direct relationship between the vapor-liquid mass transfer rates and the number of marble beds. These facts indicate that SO_2 removal is limited by liquid phase mass transfer resistance and by interfacial area, not by the equilibrium partial pressure of SO_2

(6) Increasing the total scrubber liquid-to-gas ratio decreases the sulfite supersaturation significantly but does not appear to affect the sulfate supersaturation.

5.6 Application of CE/Windsor Test Experience to EPA's Shawnee Program

One goal of the SO_2 scrubbing tests at Windsor was to gain experience in the characterization of processes that may be helpful during EPA's on-going prototype program at Shawnee. Several aspects of the sampling and data interpretation procedures used at Windsor can be related directly to the Shawnee tests. Others, particularly those dependent on relative flow rates, vessel configurations, and modes of operation, may require some modification. The single major difficulty in relating the two programs is probably the difference in test goals and proposed data interpretation procedures.

5.6.1 Sampling Procedures

The sampling procedures employed in any test must satisfy two main criteria.

- The slurry sample drawn from a vessel or process stream must be representative of the actual stream composition.

- The sampling time from when the slurry leaves the process stream to when solid-liquid separation and liquid species fixation are achieved must be small with respect to the residence time of the vessel being sampled.

Experimental results at Windsor have indicated that although sampling should be done from vertical lines to eliminate slurry stratifying effects it need not be isokinetic sampling. Non-isokinetic sampling of a 5% slurry stream induced only a 2% - 3% error. This error will vary with the percent solids and should be investigated at Shawnee before non-isokinetic sampling is employed.

Due to poor flue gas distribution the slurry composition was found to vary 20% across the bed. This sampling problem was solved by taking slurry samples from the bed front and the bed back and averaging the analysis.

To eliminate sampling errors due to reactions in the sampling lines, the sampling lines should be kept short and should be of small diameter. Care should be taken to purge the sampling lines well before samples are obtained.

Accurate pH and temperature measurements are required and should be obtained by pumping slurry directly through a small container or flow cell in which the pH electrode and thermometer are suspended. Since accurate temperature compensation is important, the pH meter should be calibrated frequently with a buffer at the same temperature as the stream to be sampled.

5.6.2 Steady State Criteria

The factors involved in determining the length of time a system must be run in a given operating mode before meaningful data can be obtained vary with the process vessel from which samples are being taken. The following steady state criteria can be established for material balance and rate calculations about the hold tank.

- A minimum period of three to four hold tank residence times must elapse before sampling (based on the total flow through the tank).
- For high solids runs where the bleed-off to the clarifier is small with respect to the total tank throughput, liquid species balances are valid after this minimum time period.

- For runs where the amount of sulfur in the liquid and solid phases is approximately equal and for solids species balances in high solids runs, at least two characteristic times based on the tank (+ scrubber) volume and clarifier bleed-off rate must elapse before sampling.

To account for short-term composition fluctuations in streams entering the hold tank at Windsor, these inlet streams were sampled three times in succession over a period of approximately one tank residence time. This allowed an average inlet composition to be calculated.

Steady state criteria for the scrubber are not as stringent since the liquid hold-up is at least an order of magnitude smaller than that of the hold tank. There should not be any significant short term fluctuation in the scrubber feed composition, but the scrubber effluent and bed should be sampled several times in succession for accurate material balances and rate calculations. For vapor-liquid equilibrium calculations in the scrubber where the liquor is sampled to calculate SO_2 partial pressures, no steady state criteria need be applied if the gas is continuously analyzed with a small lag time.

Although the entire wet scrubbing system (including clarifiers or ponds) has a very long response time, this presents no problems to material balances and rate calculations about process vessels if the system is regarded as being at "quasi-steady state" over the time period required for sampling. However the ultimate long-term performance of the system with respect to SO_2 removal and operability is a function of the eventual soluble species concentrations reached when the system reaches steady state.

5.6.3 Material Balance Data Interpretation

Total sulfur material balances were used as a check on data consistency for the Windsor wet scrubbing test series. The results of these balances are indicative of the process and analytical measurement errors that can be anticipated at Shawnee assuming similar sampling techniques are used.

The average deviation of the inlet and outlet sulfur rates for the scrubber is 7% while the majority of the deviations are within 10%. The average deviation of the inlet and outlet sulfur rates for the hold tank is 4% and the majority of the deviations are within 5%. It should be noted that the most important criterion for material balance accuracy is related to the rate calculations to be made. The absolute difference between inlet and outlet total sulfur rates should be much smaller than the amount of SO_2 removed in the scrubber if reliable precipitation rates are to be calculated.

5.6.4 Precipitation and Dissolution Rate Calculations

From observation of the rate calculations presented in Appendix E of this report, it is evident that the rates of precipitation and dissolution cannot be rigorously determined by liquid species balances alone. A combination of solid and liquid balances must be used. However, in practice it was found that rigorous calculation of precipitation and dissolution rates via solid species balances is not feasible for slurries having a solids content of greater than 2%. Even small amplitude errors in solids analyses would mask changes due to precipitation because of the high circulation rate of solids in the system.

The need for employing solid phase material balances in the rate calculations of high solids slurries (over 2%) can be eliminated by making two assumptions. For the limestone injection tests these assumptions are:

- all oxidation of aqueous SO_2 occurs in the scrubber(none in the hold tank),
- precipitation and dissolution rates of $CaCO_3$ are negligible compared to other rates of interest.

For limestone tail-end addition tests only the first assumption applies. These assumptions have been verified from experiments with low solids concentrations. It should be emphasized that these assumptions must be checked for the particular system and equipment being tested.

One objective of the Windsor test series was to relate precipitation and dissolution rates to the amounts of seed circulated in the slurry and the resulting levels of supersaturation observed. As discussed in Sections 5.4 and 5.5 of this report, for the limestone injection and the limestone tail-end addition systems the precipitation and dissolution rates were roughly proportional to the amounts of seed circulated in the slurry. Maintaining low levels of supersaturation by circulation of large amounts of seed is one approach to scale prevention.

5.6.5 SO_2 Removal in the Marble Bed Scrubber

One of the most consistent correlations developed from the Windsor test series was that relating the overall gas phase vapor-liquid mass transfer coefficient for the marble bed to the bed liquor pH. This relationship was shown in Figures 5-4, 5-7, and 5-10. Although this correlation cannot be applied directly to units other than the marble bed, similar behavior may be anticipated.

5.6.6 Prediction of Scaling Conditions

Laboratory studies have shown that scaling is related to rapid nucleation of calcium sulfite and sulfate at supersaturations exceeding the so-called "metastable limit". Experimentally determined values of relative supersaturations at which nucleation becomes significant are 1.3 - 1.4 for $CaSO_4 \cdot 2H_2O$ and 3.0 - 4.0 for $CaSO_3 \cdot \frac{1}{2}H_2O$. In general, observations of scaling during the wet scrubbing tests correlated well with experimentally determined values for the metastable limits. The sulfite limit of 3.0 - 4.0, however, did appear conservative and additional pilot data will be needed to firm up these numbers.

6.0 ANALYTICAL SUPPORT FOR SHAWNEE

Under EPA Contract CPA 70-143, Radian designed a laboratory data analysis system for EPA's demonstration of the lime/limestone wet scrubbing system at TVA's Shawnee Plant. Modifications and system improvements were conducted under this contract.

The Shawnee Laboratory Analysis System was designed to perform data storage, laboratory computations, and report generation tasks associated with the laboratory operations. The system is basically a card oriented system using marked-sense card input to ease the problem of converting data to a machine readable format. In addition, the system is designed to provide automatic operation of an X-ray fluorescence spectrometer with automatic calibration and matrix corrections performed upon the results. The X-ray analysis results are entered automatically without operator intervention.

For each set of analyses defined by a time, sampling point, sample type (i.e., line out, steady-state, or exception), and run number, a data packet is created on disk to store all raw data and computed results associated with that set of analyses. After all data for that particular set of analyses has been entered into the data processing system and all calculations performed, the completed data packet is transferred by the operator from the disk to magnetic tape and by means of the line printer a hard copy is prepared. The data analysis system may be commanded to prepare sample taking schedules and sample analysis schedules.

Analytical support for Shawnee Plant included several trips to Paducah to aid in solving hardware problems and to incorporate requested changes in the Laboratory Analysis System. The major changes to the Laboratory Analysis System were the allowance of several more default values on the card inputs to speed up the input of data to the system and the addition of several new commands implementing new analyses and allowing the input of data via CRT or teletype. In addition, Radian assisted Bechtel personnel in data tape transfer and interpretation. System capabilities were expanded to permit:

(1) dust and wet SO_2 analysis calculations, and

(2) ion imbalance calculations for the solid species.

The work done and changes made to the system are detailed in the form of trip reports in the Appendix C (see Section 10).

7.0 SOLUBILITY PRODUCT OF $CaSO_4 \cdot \frac{1}{2}H_2O$

Precipitation of calcium sulfate salts is an important aspect of lime/limestone wet scrubbing processes. Knowledge of the solubility characteristics of the various hydrated forms is necessary for an accurate description of such processes. Data for the less soluble hydration states, $CaSO_4$ (anhydrite) and $CaSO_4 \cdot 2H_2O$ (gypsum), were originally included in the Radian equilibrium model. The more soluble hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) was omitted at that time since it was not the equilibrium species in the temperature range of interest. Kinetics studies have shown, however, that the rate of hemihydrate precipitation is great compared to the rates for anhydrite and gypsum. Thus, in highly concentrated sections of the scrubber system, the solutions could become greatly supersaturated with respect to anhydrite and dihydrate and the solubility limit of the hemihydrate might be reached. Conversion to a more stable hydration state would later take place in the clarifier.

A survey was conducted to collect solubility data for calcium sulfate hemihydrate reported in the literature. These data were evaluated on the basis of experimental method and starting material employed. After selection of the best values, solubility product constants were calculated with the aid of the Radian equilibrium program and correlated in the general form shown in Equation 7-1.

$$-R\,\ell n K_T = k_1 + k_2\,\ell n T + k_3 T^{-2} + k_4 T^{-1} + k_5 T + k_6 T^2 \qquad (7\text{-}1)$$

Where R is the gas constant; K_T is the thermodynamic solubility product constant at infinite dilution; k_1, k_2, k_3, k_4, k_5, and k_6 are correlation coefficients; and T is the absolute temperature.

An investigation was made to determine the optimum number of constants so as to result in a correlation form having the least number of terms but an error still in accordance with the accuracy of the experimental data. A similar procedure was performed using all available solubility data.

7.1 Data Collection and Evaluation

Experimental solubility values for calcium sulfate hemihydrate were collected from the literature. Several solubility compilations including Gmelin (GM-001) and Linke (LI-005, LI-020) were used to obtain the data from 1950 and earlier. To locate more recent experimental evidence Chemical Abstracts was searched from 1950 through June 1971, and Chemical Titles from January to June 1971. Work relating to this subject funded by the Department of Interior's Office of Saline Water was reviewed by means of the OSW Conversion Report for the years 1969-1970 and 1971.

The selection of solubility data for $CaSO_4 \cdot \frac{1}{2}H_2O$ to be included in the Radian equilibrium program was based on the medium in which the solubility was measured, whether the metastability of the hemihydrate was taken into account in the experimental method employed, the nature of the starting material, and the care taken in the handling of the substance. The data in the temperature range 25-90°C reported by Zdanovskii and coworkers (ZD-001, ZD-002, ZD-003), Sborgi (SB-001), Riddell (RI-019), and Power et al. (PO-004, PO-022) were chosen. A second correlation was also made employing all solubility measurements reported in the literature for α-$CaSO_4 \cdot \frac{1}{2}H_2O$ determined in pure water. It should be noted that two forms of $CaSO_4 \cdot \frac{1}{2}H_2O$, the α and β forms, are possible. The α form is the most probable form encountered in lime/limestone wet scrubbing processes.

7.2 Data Correlation

Solubility data for $CaSO_4 \cdot \frac{1}{2}H_2O$ were correlated as a function of temperature (°K) in the form of Equation 7-1. A least squares technique was employed in the correlation. This technique minimizes the difference between $\ln K$ calculated and observed. The choice of $\ln K$ results in minimization of the percentage error of the correlation. The derivation of the correlation form is described in detail in Radian Technical Note 200-014-04 (see Appendix A of this report).

Solubility data for $CaSO_4 \cdot \frac{1}{2}H_2O$ collected from the literature were converted, if necessary, to weight percent $CaSO_4$ in solution. The moles of calcium, sulfate, and H_2O per 100 grams solution were then calculated for each data point and input to the Radian equilibrium program. It was then possible to determine the activities of Ca^{++}, $SO_4^=$, and H_2O which appear in the expression for the solubility product constant for $CaSO_4 \cdot \frac{1}{2}H_2O$ as shown in Equation 7-2.

$$K_T = \left(a_{Ca^{++}}\right)\left(a_{SO_4^=}\right)\left(a_{H_2O}\right)^{\frac{1}{2}} \tag{7-2}$$

This procedure was used to calculate observed solubility product constants, K_{obs}, for 18 carefully selected data points in the temperature range 25-90°C. A second run using all available data involved 59 data points in the temperature range 0-200°C.

An investigation was made to determine the optimum number of constants so as to result in a correlation having the least number of terms but an error still in accordance with the experimental data. More constants than this is a correlation of experimental error. This was accomplished by dropping k_6, k_3, k_5, and k_2 in succession from the correlation. This corresponds to elimination of the heat capacity coefficients A, B, C, and D, respectively, from Equation 7-3.

$$C_p(T) = A + BT + CT^2 - D/T \qquad (7\text{-}3)$$

k_1 and k_4 are related to the standard entropy and enthalpy for the reaction of interest, the dissolution of calcium sulfate hemihydrate.

The relationships between the heat capacity coefficients, the standard state entropy and enthalpy, and the correlation coefficients are fully described in Radian Technical Note 200-014-04. Basically, integration of Equation 7-3, substitution of temperature limits, substitution of $\Delta H^\circ_{R\ 298}$ and $\Delta S^\circ_{R\ 298}$ for thermodynamically equivalent terms, and collection of like terms result in an equation having the same general form as Equation 7-1. The forms of the coefficients k_i are shown below.

$$k_1 = -\Delta S^\circ_{R\ 298} + \Delta A(\ell n\ 298.16 + 1) + \Delta B(298.16) + (\tfrac{1}{2})(298.16)^2\Delta C + (\tfrac{1}{2})\frac{\Delta D}{(298.16)^2} \qquad (7\text{-}4a)$$

$$k_2 = \Delta A \qquad (7\text{-}4b)$$

$$k_3 = (\tfrac{1}{2})\Delta D \qquad (7\text{-}4c)$$

$$k_4 = \Delta H^\circ_{R\ 298} - 298.16\ \Delta A - \frac{(298.16)^2}{2}\Delta B - \frac{(298.16)^3}{3}\Delta C - \left(\frac{1}{298.16}\right)\Delta D \qquad (7\text{-}4d)$$

$$k_5 = (-\tfrac{1}{2})\Delta B \qquad (7\text{-}4e)$$

$$k_6 = (-1/3)\Delta C \qquad (7\text{-}4f)$$

The results of this investigation using the selected data from 25-90°C are given in Table 7-1. The root mean square (RMS) error for the correlation is also given for each case. This number was also used to compare the accuracy of the correlation with the experimental error. A second correlation was also made for 59 data points which included solubility data for $CaSO_4 \cdot \frac{1}{2}H_2O$ in the range 0-200°C.

7.3 Results

The k's calculated in Case 3 have been selected as the set of coefficients to be used in the calculation of solubility product constants in the Radian equilibrium program. This choice was made on the basis of constancy of the RMS error and enthalpy and entropy terms in Cases 1, 2, and 3 as the coefficients none, C, and C and D, respectively, were eliminated from the correlation. The correlation error of ~5% is reasonable with respect to the solubility data selected from the literature. Table 7-2 gives the tabulated results of Case 3, including the raw solubility data in weight percent $CaSO_4$ in solution at each temperature, observed and calculated solubility product constants, the error fraction $(K_{obs} - K_{calc})/K_{obs}$, and the literature reference for each data point.

In summary, the solubility product constant for $\alpha - CaSO_4 \cdot \frac{1}{2}H_2O$ may be expressed the relationship:

$$-R \ln K_T = -81.826056 + 12.707705 \ln T + 3429.0616\ T^{-1} + 0.054204619\ T \qquad (7\text{-}5)$$

TABLE 7-1

RESULTS OF INVESTIGATION TO DETERMINE OPTIMUM NUMBER OF CONSTANTS FOR CORRELATION

Case	Heat Capacity Coefficients Included	RMS Error	$\Delta H^\circ_{R_{298}}$	$\Delta S^\circ_{R_{298}}$	ΔA	ΔB	ΔC	ΔD
1	A, B, C, D,	0.05024	-5.169×10^{3}	-35.58	+ 1.457	-6.754×10^{-2}	-3.163×10^{-4}	-4.017×10^{5}
2	A, B, D	0.05028	-5.094×10^{3}	-35.33	+ 1.312	-1.089×10^{-1}	0	$+1.700\times10^{2}$
3	A, B	0.05030	-5.178×10^{3}	-35.60	-12.71	-1.084×10^{-1}	0	0
4	A	0.05090	-5.355×10^{3}	-36.17	-39.95	0	0	0
5	None	0.7742	-2.530×10^{-5}	-19.74	0	0	0	0

TABLE 7-2

RESULTS OF CORRELATION OF 25-90°C DATA

	Degrees Centigrade	Degrees Kelvin	$CaSO_4$-1/2 H_2O Solubility Gram/100 G Soln	Solubility Product Constant (g-moles/kg $H_2O)^2$ Observed	Calculated	Error Fraction	Reference
1	25.0	298.2	.6940	.10072867-03	.10320439-03	-.246-01	ZD-003
2	25.0	298.2	.7100	.10340530-03	.10320439-03	.194-02	SB-001
3	25.0	298.2	.6620	.95396033-04	.10320439-03	-.819-01	ZD-001
4	25.0	298.2	.7850	.11603980-03	.10320439-03	.111	ZD-002
5	31.0	304.2	.5980	.81248368-04	.86470887-04	-.643-01	RI-019
6	35.0	308.2	.6030	.79536831-04	.76768214-04	.348-01	SB-001
7	40.0	313.2	.5500	.68685806-04	.66081333-04	.379-01	SB-001
8	45.0	318.2	.4552	.52893859-04	.56815099-04	-.741-01	PO-004
9	50.0	323.2	.4560	.50668615-04	.48794536-04	.370-01	ZD-003
10	50.0	323.2	.4270	.46963430-04	.48794536-04	-.390-01	RI-019
11	50.0	323.2	.4700	.52465375-04	.48794536-04	.700-01	SB-001
12	50.0	323.2	.4360	.48110833-04	.48794536-04	-.142-01	ZD-001
13	65.0	338.2	.3280	.29847979-04	.30728143-04	-.295-01	PO-004
14	75.0	348.2	.2900	.23210667-04	.22479702-04	.315-01	ZD-003
15	75.0	348.2	.2710	.21451469-04	.22479702-04	-.479-01	RI-019
16	75.0	348.2	.2900	.23210667-04	.22479702-04	.315-01	SB-001
17	75.0	384.2	.2860	.22839388-04	.22479702-04	.157-01	ZD-001
18	84.0	357.2	.2380	.16617612-04	.16925249-04	-.185-01	PO-004

RMS Error For This Case = .5030-01

k_1 = -81.826056
k_2 = 12.707705
k_4 = 3429.0616
k_5 = .54204619-01

8.0 NOMENCLATURE AND UNITS CONVERSION

8.1 Nomenclature

a	interfacial area
a_i	chemical activity of $i^{\underline{th}}$ species
A	temperature independent constant in Arrhenius relationship
A_o	initial value of surface area
A,B,C,D	heat capacity coefficients
C	concentration
ΔC	change in concentration
C_{in}	initial concentration
C_p	heat capacity
E^*	activation energy
F	flow rate
G	gas flow rate
$\Delta H_{R\ 298}$	standard state enthalpy
k	rate constant
k_i	coefficients in solubility product correlation
K_G	overall gas phase mass transfer coefficient
K_{sp}	solubility product constant
K_T	themodynamic solubility product constant
M	mass of seeds
M_o	initial mass of seeds
n	number of seed crystals; also $n_+ + n_-$
n_+, n_-	number of cations and anions
NTU	number of transfer units
P	pressure
r	relative saturation

R	reaction rate; also gas constant
ΔS	difference in amounts of sulfur
$\Delta S_{R\,298}$	standard state entropy
t	time
T	absolute temperature
V	volume
y	mole fraction of SO_2 in the gas phase
y*	mole fraction of SO_2 in the gas phase in equilibrium with liquid phase
α	crystalline form of $CaSO_4 \cdot \frac{1}{2}H_2O$
β	undetermined coefficients
γ	activity coefficient
ϕ	some function of actual and equilibrium concentrations or activities of the reacting species

8.2 Units Conversion

Engineering quantities presented in this report are expressed in English units, i.e., inches, feet, gallons, SCFH, °F, psia, etc. Conversion factors for determining the metric equivalent of each of these quantities are listed below:

1 ACFM = 28.316 liters/minute
1 foot = 0.30480 meters
1 ft^2 = 0.092903 square meters
1 ft^3 = 28.316 liters
1 gallon = 3.7853 liters
1 inch = 2.5400 centimeters
1 lb-mole = 453.59 g-moles
1 psia = 5.1715 cm Hg
1 SCFH = 28.316 standard liters/minutes

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10.0 APPENDICES

10.1 APPENDIX A

RADIAN TECHNICAL NOTE 200-014-04

CALCIUM SULFATE HEMIHYDRATE SOLUBILITY

TECHNICAL NOTE 200-014-04

CALCIUM SULFATE HEMIHYDRATE SOLUBILITY

12 November 1971

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1.0 INTRODUCTION

Precipitation of calcium sulfate salts is an important aspect of lime/limestone wet scrubbing processes. Knowledge of the solubility characteristics of the various hydrated forms is necessary for an accurate description of such processes. Data for the less soluble hydration states, $CaSO_4$ (anhydrite) and $CaSO_4 \cdot 2H_2O$ (gypsum), were originally included in the Radian equilibrium model. The more soluble hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) was omitted at that time since it was not the equilibrium species in the temperature range of interest. Kinetics studies have shown, however, that the rate of hemihydrate precipitation is great compared to the rates for anhydrite and gypsum. Thus, in highly concentrated sections of the scrubber system, the solutions could become greatly supersaturated with respect to zero and dihydrate, and the solubility limit of the hemihydrate might be reached. Conversion to a more stable hydration state would later take place in the clarifier.

A survey was conducted to collect solubility data for calcium sulfate hemihydrate reported in the literature. These data were evaluated on the basis of experimental method and starting material employed. After selection of the best values, solubility product constants were calculated with the aid of the Radian equilibrium program and correlated in the general form shown in Equation 1-1.

$$-R\ell nK = k_1 + k_2' \ell nT + k_3 T^{-2} + k_4 T^{-1} + k_5 T + k_6 T^2 \qquad (1\text{-}1)$$

An investigation was made to determine the optimum number of constants so as to result in a correlation form having the least number of terms but an error still in accordance with the experimental data. A similar procedure was carried out using all available solubility data.

The following sections of this technical note describe the collection, evaluation, and correlation of data which have been carried out.

2.0 DATA COLLECTION

Experimental solubility values for calcium sulfate hemihydrate were collected from the literature. Several solubility compilations including Gmelin (GM-001) and Linke (LI-005, LI-020) were used to obtain the data from 1950 and earlier. To locate more recent experimental evidence *Chemical Abstracts* was searched from 1950 through June, 1971, and *Chemical Titles* from January to June 1971. Work relating to this subject funded by the Office of Saline Water was reviewed by means of the *OSW Conversion Report* for the years 1969-1970 and 1971. Copies of approximately 20 articles and 40 abstracts were added to the Radian literature system.

3.0 DATA EVALUATION

3.1 Controversy Concerning Number of Crystalline Phases

The exact number of distinct crystalline forms of $CaSO_4 \cdot \frac{1}{2}H_2O$ was found to be in dispute in the literature; opinions varied from zero to two. Ridge and Beretka (RI-003) and Rabinowitz, *et al.*, (RA-028) have summarized much of the evidence presented thus far.

Early investigators regarded the hemihydrate as a zeolitic hydrate of γ-$CaSO_4$ and not as a distinct crystalline species. Some crystallographic data were cited which supported this viewpoint. Improved experimental techniques later proved that the hemihydrate and γ-$CaSO_4$ did have distinguishable powder patterns.

The different properties of the two postulated forms of hemihydrate are due chiefly to their methods of preparation. The α-form is prepared by a wet method, usually autoclaving the dihydrate for five to six hours at a pressure of 20 lb/in². Other techniques are also practiced. This type of procedure results in well-formed crystals of low porosity. The dry method of preparation involves dry-calcining gypsum in an oven at 150°C. The hemihydrate produced, commonly referred to as β-$CaSO_4 \cdot \frac{1}{2}H_2O$, is characterized by relatively small crystallite size, large surface area, and a high degree of porosity. Ridge points out that the smaller crystal size could be responsible for the greater solubility of this form, as reported by Zdanovskii and co-worker (ZD-001, ZD-002, ZD-003)*. Table 3-1 gives a comparison of the solubilities of these two forms as reported by these workers. If this were the case, then solubility differences could not be used as evidence for the existence of two crystalline species. Other characteristics often used as criteria for distinctiveness such as X-ray and electron diffraction, infrared absorption, and proton magnetic resonance absorption, have failed to show conclusively that two structural forms exist.

In this investigation, solubility data were collected for both postulated forms when available. However, since the

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* In one publication by Zdanovskii (ZD-001), the labeling of the graphs and tables showing α and β-$CaSO_4 \cdot \frac{1}{2}H_2O$ solubility has apparently been reversed.

TABLE 3-1

SOLUBILITIES OF α- AND β-$CaSO_4 \cdot \frac{1}{2}H_2O$ IN WATER AT VARIOUS TEMPERATURES

	Solubility in Weight Percent $CaSO_4$	
T°C	α-$CaSO_4 \cdot \frac{1}{2}H_2O$	β-$CaSO_4 \cdot \frac{1}{2}H_2O$
0	0.986	1.060
25	0.694	0.762
50	0.456	0.494
75	0.290	0.306
100	0.200	0.208

Reference: ZD-003

dry-calcined form (β) is more soluble and upon contact with water hydrates more rapidly than the α-form, it was necessary to make a choice of which data to use in our correlation. The α-form was selected on the basis that it would be the form most probably encountered in a wet scrubbing process. Also, the data reported for this form was in close agreement with values given for unclassified hemihydrate.

3.2 Experimental Method

Several different methods have been applied to the determination of calcium sulfate hemihydrate solubility as reported in the literature. The metastability of this compound in the $CaSO_4$-H_2O system causes some doubt as to the accuracy of measurements obtained from standard procedures for solubility determinations. A description of the various methods which have been applied is given below.

1. Kinetic Method

The kinetic method of solubility determination was used by Zdanovskii and co-workers (ZD-001, ZD-002, ZD-003) to measure the solubilities of powdered materials. Several samples of equal weights were dissolved in succession in the same volume of water or solution containing from 0.1 to 0.5% $CaSO_4$. Uniform conditions of stirring and temperature were maintained. A specified amount of time was allowed for dissolution, followed by immediate withdrawal, filtration, and analysis of solution specimens, which yielded the increase in concentration of $CaSO_4$ in solution.

Increase in $CaSO_4$ concentration was plotted *versus* initial $CaSO_4$ concentration in the solution for a given temperature. Intersection of the isochrone with the abscissa (the point at which the increase in concentration of dissolved $CaSO_4$ is zero) axis yielded the solubility of the hemihydrate at that temperature. A second and, in some cases, a third isochrone acted as a check on the result obtained from the first.

Different variants were used in the studies described, and are summarized in Table 3-2.

2. Conductometric Method

As a salt dissolves, the electrical conductivity of the solution increases in proportion to the amount of ions present. This is the principle of the method used by Sborgi and Bianchi (SB-001) and Smith (as reported by Player, PL-007). At each temperature the conductance of the solution is measured as a function of time. The point of maximum conductance is taken as the solubility at that temperature. The composition of the solution at that point is determined by chemical analysis of a filtered sample.

TABLE 3-2

EXPERIMENTAL CONDITIONS OF SOLUBILITY STUDIES CONDUCTED BY KINETIC METHOD

Reference	Salt	Medium	Temperature Range	Sample Weight (in grams)	Amount of Solvent	Initial Concentration of Solvent with $CaSO_4$	Dissolutio Time (minutes)
ZD-001	α- and β-hemihydrates	water	0-100°C	1-2	200 ml	0.1 - 0.5%	5, 10, 15
ZD-002	α- and β-hemihydrates; dehydrated α- and β-hemihydrates; soluble α- and β-anhydrite; insoluble anhydrite	0-40% H_2SO_4	25	4	100 ml	0.2 - 0.6%	3, 5
ZD-003	α- and β-hemihydrates; dehydrated α- and β-hemihydrates; soluble α- and β-anhydrite; insoluble anhydrite	water	0-100°C	4	100 g	0.1 - 0.5%	3, 5

3. Isothermal Method

The standard isothermal method for determining solubilities has been applied to calcium sulfate hemihydrate by some investigators (PO-004). The temperature of a specified volume of distilled water or, in some cases, a filtered saturated $CaSO_4$ solution is held constant throughout the run. A weighed sample of hemihydrate is added to the stirred solvent. Samples of solid and liquid phases are taken regularly for analysis. The hydrate water content of the solid phase is analyzed by gravimetry (loss-on-ignition method). The calcium sulfate content of the solution is determined by an EDTA titration of Ca^{++}. Power and co-workers (PO-004) simultaneously carried out conductometric measurements during the run to locate solubility maxima, which were taken as the solubility of the substance.

3.3 Nature of the Starting Material

Another criterion in the selection of our data was the nature of the starting material. This was important for several reasons. As described in Section 3.1, the method of preparation of the hemihydrate has a great effect on the physical properties of the product. Therefore if the investigator failed to describe how the starting material was prepared, his results became questionable. Also the handling of the starting material could influence the reliability of the data. In some earlier investigations data incorrectly assigned to "soluble anhydrite" prepared by complete dehydration of gypsum were in error because of the rapid rehydration to hemihydrate on exposure to the atmosphere.

The selection of solubility data for $CaSO_4 \cdot \frac{1}{2}H_2O$ to be included in the Radian equilibrium program was thus based on whether the metastability of the hemihydrate was taken into account in the experimental method employed, the nature of the starting material, and the care taken in the handling of the substance. The data in the temperature range 25-90°C reported by Zdanovskii and co-workers (ZD-001, ZD-002, ZD-003), Sborgi (SB-001), Riddell (RI-019), and Power, et al., (PO-004, PO-022) were chosen. The results of the selected 25-90°C data correlation, which is described in the following section, give an approximate error of 5% compared to an 11% error when all available data in the range 0-200°C for hemihydrate prepared by a wet method were used.

4.0 DATA CORRELATION

Solubility data for $CaSO_4 \cdot \frac{1}{2}H_2O$ were correlated as a function of temperature (°K) in the form of Equation 4-1 using a least squares technique.

$$-R\ln K_T = k_1 + k_2 \ln T + k_3 T^{-2} + k_4 T^{-1} + k_5 T + k_6 T^2 \qquad (4\text{-}1)$$

The observed solubility product constants, K_{obs}, were calculated from reported solubility data using the Radian equilibrium program. The least squares technique minimized the difference between $\ln K$ calculated and observed. The choice of $\ln K$ results in minimization of the percentage error of the correlation. An investigation was made to determine the optimum number of constants so as to result in a correlation having the least number of terms but an error still in accordance with the experimental data. Section 4.3 describes this aspect of the study, and Sections 4.1 and 4.2 give a description of the calculation of K_{obs} and the derivation of the general correlation form respectively.

4.1 Calculation of Observed Solubility Product Constant

Solubility data for $CaSO_4 \cdot \frac{1}{2}H_2O$ collected from the literature were converted, if necessary, to weight percent $CaSO_4$ in solution. The moles of CaO, SO_3, and H_2O per 100 grams solution were then calculated for each data point and input to the Radian equilibrium program. It was then possible to determine the activities of Ca^{++}, $SO_4^=$, and H_2O which appear in the expression for the solubility product constant for $CaSO_4 \cdot \frac{1}{2}H_2O$ as shown in Equation 4-2.

$$K_{sp} = \left(a_{Ca^{++}}\right)\left(a_{SO_4^=}\right)\left(a_{H_2O}\right)^{\frac{1}{2}} \qquad (4\text{-}2)$$

This procedure was used to calculate observed solubility product constants, K_{obs}, for 18 carefully selected data points in the range 25-90°C. A second run using all available data involved 59 data points.

4.2 Derivation of Correlation Form

This section describes how the equilibrium constant for a reaction can be calculated. The reaction of interest is the dissolution of calcium sulfate hemihydrate as shown in Equation 4-3.

$$CaSO_4 \cdot \tfrac{1}{2}H_2O_{(s)} \rightleftarrows Ca^{++} + SO_4^= + \tfrac{1}{2}H_2O_{(\ell)} \qquad (4\text{-}3)$$

This general reaction can be described by Equation 4-4, with i reactants and products where α_{ij} and β_{ij} are the stoichiometric coefficients.

$$\sum_i \alpha_{ij} \text{ Reactants} \rightleftarrows \sum_i \beta_{ij} \text{ Products} \qquad (4\text{-}4)$$

Note that when i is a reactant, $\beta_i = 0$ and when i is a product, $\alpha_i = 0$. At equilibrium and at temperature T, Equation 4-5 holds.

$$\Delta G^\circ_T = \Delta H^\circ_T - T\Delta S^\circ_T \qquad (4\text{-}5a)$$

$$\Delta G^\circ_T = -RT\ell nK_T \qquad (4\text{-}5b)$$

$$\ell nK_T = -\frac{1}{R}\left(\frac{\Delta H^\circ_T}{T} - \Delta S^\circ_T\right) \qquad (4\text{-}5c)$$

Thus, the equilibrium constant for a reaction at temperature T may be calculated by evaluating the right hand side of Equation 4-5c. The enthalpy term is evaluated from Equation 4-6 and likewise, the entropy term from Equation 4-7.

$$\Delta H^\circ_{T_j} = \sum_i \left\{\beta_{ij}\left[\Delta H^\circ_{f_{298_i}} + \int_{298}^{T} Cp(T)_i dT\right] - \alpha_{ij}\left[\Delta H^\circ_{f_{298_i}} + \int_{298}^{T} Cp(T)_i dT\right]\right\}$$

$$= \sum_i \left(\beta_{ij} - \alpha_{ij}\right)\left[\Delta H^\circ_{f_{298_i}} + \int_{298}^{T} Cp(T)_i dT\right] \qquad (4\text{-}6)$$

$$\Delta S^\circ_{T_j} = \sum_i \left\{\beta_{ij}\left[S^\circ_{298_i} + \int_{298}^{T} \frac{Cp(T)_i}{T} dT\right] - \alpha_{ij}\left[S^\circ_{298_i} + \int_{298}^{T} \frac{Cp(T)_i}{T} dT\right]\right\}$$

$$= \sum_i \left(\beta_{ij} - \alpha_{ij}\right)\left[S^\circ_{298_i} + \int_{298}^{T} \frac{Cp(T)_i}{T} dT\right] \qquad (4\text{-}7)$$

The form of Cp(T) for both products and reactants is given in Equation 4-8.

$$Cp(T) = A + BT + CT^2 - D/T^2 \qquad (4\text{-}8)$$

Integrating the heat capacity terms, substituting the temperature limits, substituting ΔH°_T and ΔS°_T in Equation 4-5c, and collecting like terms result in an equation of the following form:

$$-R\ln K_T = k_1 + k_2 \ln T + k_3 T^{-2} + k_4 T^{-1} + k_5 T + k_6 T^2 \qquad (4\text{-}9)$$

The form of the constants k_1 through k_6 is given below.

$$k_1 = (-1) \sum_i \left(\beta_{ij} - \alpha_{ij}\right) S^\circ_{298_i} + \Delta A(\ln 298.16 + 1)$$

$$+ \Delta B(298.16) + (\tfrac{1}{2})(298.16)^2 \Delta C + (\tfrac{1}{2}) \frac{\Delta D}{(298.16)^2} \qquad (4\text{-}10a)$$

$$k_2 = -\Delta A \qquad (4\text{-}10b)$$

$$k_3 = (\tfrac{1}{2})\Delta D \qquad (4\text{-}10c)$$

$$k_4 = \left[\sum_i \left(\beta_{ij} - \alpha_{ij}\right) \Delta H^\circ_{f_{298_i}} \right] - 298.16\ \Delta A - \frac{(298.16)^2}{2} \Delta B$$

$$- \frac{(298.16)^3}{3} \Delta C - \left(\frac{1}{298.16}\right) \Delta D \qquad (4\text{-}10d)$$

$$k_5 = (-\tfrac{1}{2})\Delta B \qquad (4\text{-}10e)$$

$$k_6 = (-\tfrac{1}{6})\Delta C \qquad (4\text{-}10f)$$

where:

$$\Delta A = \sum_i \left(\beta_{ij} - \alpha_{ij}\right) A_i \qquad (4\text{-}11a)$$

$$\Delta B = \sum_i \left(\beta_{ij} - \alpha_{ij}\right) B_i \qquad (4\text{-}11b)$$

$$\Delta C = \sum_i \left(\beta_{ij} - \alpha_{ij}\right) C_i \qquad (4\text{-}11c)$$

$$\Delta D = \sum_i \left(\beta_{ij} - \alpha_{ij}\right) D_i \qquad (4\text{-}11d)$$

4.3 Determination of Optimum Number of Constants to be Used in Correlation

An investigation was carried out to determine the optimum number of constants so as to result in a correlation having the fewest constants but an error still in accordance with the experimental data. This was accomplished by dropping k_6, k_3, k_5, and k_2 in succession from the correlation. As shown in Equations 4-10a through 4-10f this corresponds to elimination of C, D, B, and A respectively from the heat capacity equation. Substituting the values calculated for the remaining k's in Equations 4-10a - 4-10f yielded ΔA, ΔB, ΔC, ΔD, and the enthalpy and entropy changes for the reaction of interest (Equation 4-3) at 298°K. The enthalpy change for this reaction is the standard heat of solution for calcium sulfate hemihydrate, i.e., from solid to infinite dilution. This number should be constant and was used as a criterion for the accuracy of the correlation. If too many constants had been dropped from the correlation then the value of $\Delta H^{\circ}_{S_{298}}$ for that case would be noticeably different from $\Delta H^\circ_{S_{298}}$ values resulting from cases which included a greater number of constants. The entropy change for the reaction as it appears in Equation 4-10a, the expression for k_1, was similarly used.

The results of this investigation using the selected data from 25-90°C are given in Table 4-1. The root mean square (RMS) error for the correlation is also given for each case. This number was also used to compare the accuracy of the correlation with the experimental error.

A second correlation was made which included solubility data for calcium sulfate hemihydrate in the range 0-200°C. Only data measured clearly using the β-hemihydrate (dry-calcined gypsum) were excluded; this screening was done because of the noticeably greater solubility of this form compared to the hemihydrate prepared by a wet method. As mentioned in Section 3.1 this property is not necessarily evidence of its existence as a distinct crystalline species but rather may be due to its smaller crystallite size and greater porosity. If the identity of the starting material was not clear, but the results seemed consistent with other reported values for the α-form, the data were included. As shown in Table 4-2, omission of correlation constants produced results corresponding to the previously described study, but with much larger RMS errors (~ 11%) and greater deviations in the other calculated values.

TABLE 4-1

Case	Heat Capacity Coefficients Included	RMS Error	$\Delta H^\circ_{R_{298}}$	$\Delta S^\circ_{R_{298}}$	ΔA	ΔB	ΔC	ΔD
1	A, B, C, D	0.05024	$-5.169\text{x}10^{3}$	-35.58	+ 1.457	$-6.754\text{x}10^{-2}$	$-3.163\text{x}10^{-4}$	$-4.017\text{x}10^{5}$
2	A, B, D	0.05028	$-5.094\text{x}10^{3}$	-35.33	+ 1.312	$-1.089\text{x}10^{-1}$	0	$+1.700\text{x}10^{6}$
3	A, B	0.05030	$-5.178\text{x}10^{3}$	-35.60	-12.71	$-1.084\text{x}10^{-1}$	0	0
4	A	0.05090	$-5.355\text{x}10^{3}$	-36.17	-39.95	0	0	0
5	None	0.7742	$-2.530\text{x}10^{-5}$	-19.74	0	0	0	0

TABLE 4-2

Case	Heat Capacity Coefficients Included	RMS Error	$\Delta H^\circ_{R_{298}}$	$\Delta S^\circ_{R_{298}}$	ΔA	ΔB	ΔC	ΔD
1	A, B, C, D	0.1108	$-4.278\text{x}10^{3}$	-32.65	-11.50	$+8.831\text{x}10^{-2}$	$-6.499\text{x}10^{-4}$	$+3.068\text{x}10^{6}$
2	A, B, D	0.1103	$-4.301\text{x}10^{3}$	-32.74	+13.79	$-2.800\text{x}10^{-1}$	0	$+2.849\text{x}10^{5}$
3	A, B	0.1104	$-4.325\text{x}10^{3}$	-32.83	+14.29	$-2.875\text{x}10^{-1}$	0	0
4	A	0.1158	$-4.238\text{x}10^{3}$	-32.43	-85.66	0	0	0
5	None	14.80	$-5.308\text{x}10^{-4}$	-22.95	0	0	0	0

5.0 RESULTS

The k's calculated in Case 3 in the first series of correlations have been selected as the set of coefficients to be used in the calculation of solubility product constants in the Radian equilibrium program. This choice was made on the basis of consistency of the RMS error and enthalpy and entropy terms in Cases 1, 2, and 3 as the coefficients none, C, and C and D, respectively, were eliminated from the correlation. The correlation error of ~ 5% is reasonable with respect to the solubility data selected from the literature. Table 5-1 gives the tabulated results of Case 3, including the raw solubility data in weight percent $CaSO_4$ in solution at each temperature, observed and calculated solubility product constants, the error fraction $(K_{obs} - K_{calc})/k_{obs}$, and the literature reference for each data point.

Table 5-2 is the tabulation of results from the correlation using the data in the 0-200°C range. Again, Case 3 is shown in which the A and B coefficients in the heat capacity equation were used.

TABLE 5-1

	TEMPERATURE DEGREES CENTIGRADE	TEMPERATURE DEGREES KELVIN	CASO4-1/2 H2O SOLUBILITY GRAM/100 G SOLN	SOLUBILITY PRODUCT CONSTANT (GMOLES/KG H2O)**2 OBSERVED	SOLUBILITY PRODUCT CONSTANT (GMOLES/KG H2O)**2 CALCULATED	ERROR FRACTION	REFERENCE
1	25.0	298.2	.6940	.10072867-03	.10320439-03	-.246-01	ZD-003
2	25.0	298.2	.7100	.10340539-03	.10320439-03	.194-02	SB-001
3	25.0	298.2	.6620	.95396033-04	.10320439-03	-.819-01	ZD-001
4	25.0	298.2	.7850	.11603980-03	.10320439-03	.111	ZD-002
5	31.0	304.2	.5980	.81248368-04	.86470887-04	-.643-01	KI-019
6	35.0	308.2	.[illegible]30	.79536851-04	.76766214-04	.349-01	SB-001
7	40.0	313.2	.5500	.68685806-04	.66081333-04	.379-01	SB-001
8	45.0	318.2	.4552	.52893859-04	.56815099-04	-.741-01	PO-004
9	50.0	323.2	.4560	.50668615-04	.48794536-04	.370-01	ZD-003
10	50.0	323.2	.4270	.46963430-04	.48794536-04	-.390-01	KI-019
11	50.0	323.2	.4700	.52465375-04	.48794536-04	.700-01	SB-001
12	50.0	323.2	.4360	.48110833-04	.48794536-04	-.142-01	ZD-001
13	65.0	338.2	.3280	.29847979-04	.30728143-04	-.295-01	PO-004
14	75.0	348.2	.2900	.23210667-04	.22479702-04	.315-01	ZD-003
15	75.0	348.2	.2710	.21451469-04	.22479702-04	-.479-01	KI-019
16	75.0	348.2	.2900	.23210667-04	.22479702-04	.315-01	SB-001
17	75.0	348.2	.2860	.22839388-04	.22479702-04	.157-01	ZD-001
18	84.0	357.2	.2380	.16617612-04	.16925249-04	-.185-01	PO-004

RMS ERROR FOR THIS CASE = .5030-01

k_1 = -81.826056
k_3 = 12.707705
k_4 = 3429.0516
k_8 = .54204619-01

TABLE 5-2

	TEMPERATURE		CASO4-1/2 H2O	SOLUBILITY PRODUCT CONSTANT (G-MOLES/KG H2O)**2		ERROR	REFERENCE
	DEGREES CENTIGRADE	DEGREES KELVIN	SOLUBILITY GRAM/100 G SOLN	OBSERVED	CALCULATED	FRACTION	
1	.0	273.2	.9860	.17350193-03	.16912467-03	.252-01	ZD-003
2	3.0	276.2	.8250	.13339222-03	.16014683-03	-.149	RI-019
3	5.0	278.2	1.10 *****	.19258572-03	.15419988-03	.199	SB-001
4	11.0	284.2	.7490	.11989450-03	.13671171-03	-.140	RI-019
5	18.0	291.2	.8200	.12701368-03	.11733672-03	.820-01	SB-001
6	21.5	294.7	.6620	.97662481-04	.10818923-03	-.108	RI-019
7	23.5	296.7	.6530	.94665785-04	.10314459-03	-.873-01	RI-019
8	25.0	298.2	.6940	.10072867-03	.99452379-04	.127-01	ZD-003
9	25.0	298.2	.7100	.10340530-03	.99452379-04	.382-01	SB-001
10	25.0	298.2	.6620	.95396033-04	.99452379-04	-.425-01	ZD-001
11	25.0	298.2	.7850	.11603980-03	.99452379-04	.143	ZD-002
12	31.0	304.2	.5980	.61248368-04	.85501808-04	-.524-01	RI-019
13	35.0	308.2	.6030	.79536831-04	.76952948-04	.325-01	SB-001
14	40.0	313.2	.5500	.65685806-04	.67126500-04	.227-01	SB-001
15	45.0	318.2	.4552	.52693859-04	.58247074-04	-.101	PO-004
16	50.0	323.2	.4560	.50668615-04	.50287395-04	.752-02	ZD-003
17	50.0	323.2	.4270	.46563430-04	.50287395-04	-.708-01	RI-019
18	50.0	323.2	.4700	.52465375-04	.50287395-04	.415-01	SB-001
19	50.0	323.2	.4360	.49110833-04	.50287395-04	-.452-01	ZD-001
20	65.0	338.2	.3280	.29847979-04	.31456427-04	-.539-01	FO-004

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TABLE 5-2 (cont.)

21	75.0	348.2	.2900	.23210667-04	.22511437-04	.301-01	ZO-003
22	75.0	348.2	.2710	.21451469-04	.22511437-04	-.494-01	RI-019
23	75.0	348.2	.2900	.23210667-04	.22511437-04	.301-01	SB-001
24	75.0	348.2	.2860	.22839388-04	.22511437-04	.144-01	ZO-001
25	84.0	357.2	.2380	.16617612-04	.16432074-04	.112-01	PO-004
26	93.0	366.2	.1930	.11654957-04	.11850516-04	-.168-01	RI-019
27	95.0	368.2	.1982	.11723530-04	.11003046-04	.615-01	PO-022
28	100.0	373.2	.2000	.11104169-04	.91183093-05	.179	ZO-003
29	100.0	373.2	.1764	.95937536-05	.91183093-05	.496-01	PO-022
30	100.0	373.2	.1645	.88394401-05	.91183093-05	-.315-01	PA-024
31	100.0	373.2	.1090	.10397931-04	.91183093-05	.123	SB-001
32	100.0	373.2	.1980	.10975489-04	.91183093-05	.169	ZO-001
33	100.5	373.7	.1600	.85005358-05	.89469310-05	-.525-01	PO-026
34	105.0	378.2	.1499	.74218575-05	.75315459-05	-.148-01	PO-004
35	106.0	379.2	.1480	.72147189-05	.72459491-05	-.433-02	SV-012
36	110.0	383.2	.1510	.69970473-05	.62006517-05	.114	SB-001
37	110.0	383.2	.1290	.58150781-05	.62006517-05	-.663-01	PA-024
38	114.0	387.2	.1250	.53048433-05	.52956257-05	.174-02	SV-012
39	115.0	388.2	.1120	.45951140-05	.50892674-05	-.108	HA-062
40	120.0	393.2	.1030	.39810599-05	.41645804-05	-.731-01	PA-024
41	122.0	395.2	.1010	.36862072-05	.38404569-05	-.418-01	HA-062

TABLE 5-2 (cont.)

42	125.0	398.2	.0955	.33046439-05	.33980352-05	-.282-01	PA-072
43	130.0	403.2	.0890	.28276894-05	.27648152-05	.220-01	SP-012
44	130.0	403.2	.0830	.26026296-05	.27648152-05	-.623-01	PA-024
45	134.0	407.2	.0703	.20138315-05	.23397262-05	-.162	FO-022
46	136.0	409.2	.0773	.21684252-05	.21509856-05	.173-01	FO-022
47	140.0	413.2	.0779	.20789033-05	.18156806-05	.127	TI-011
48	140.0	413.2	.0665	.17238070-05	.18156806-05	-.533-01	PA-024
49	142.0	415.2	.0650	.16276121-05	.16671461-05	-.243-01	HA-062
50	146.0	421.2	.0431	.90736181-06	.12874642-05	-.419	FO-022
51	150.0	423.2	.0530	.11288930-05	.11802725-05	-.455-01	PA-024
52	160.0	433.2	.0415	.72057144-06	.75990602-06	-.546-01	PA-024
53	165.0	438.2	.0560	.94556511-06	.60766446-06	.357	TI-011
54	170.0	443.2	.0325	.45813861-06	.48485957-06	-.583-01	PA-024
55	180.0	453.2	.0225	.25009817-06	.30674267-06	-.226	PA-024
56	160.0	453.2	.0270	.31150940-06	.30674267-06	.153-01	TI-011
57	186.0	459.2	.0260	.26933283-06	.23215628-06	.138	HA-062
58	190.0	463.2	.0205	.18954399-06	.19250427-06	-.156-01	PA-024
59	200.0	473.2	.0165	.12332889-06	.11989593-06	.278-01	PA-024

RMS ERROR FOR THIS CASE = .1104

k_1 = 42.794428
k_3 = -14.238249
k_4 = 4194.2512
k_5 = .14375275

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10.2 APPENDIX B

RADIAN TECHNICAL NOTE 200-014-07

DISSOLUTION KINETICS
LITERATURE REVIEW AND SCREENING EXPERIMENTS

TECHNICAL NOTE 200-014-07

DISSOLUTION KINETICS
LITERATURE REVIEW AND SCREENING EXPERIMENTS

30 May 1972

Prepared by:
James L. Phillips

1.0 INTRODUCTION

This technical note reviews previous work in the area of dissolution kinetics. An initial series of experiments to screen for rate-limiting regimes governing dissolution of $CaCO_3$ in aqueous solutions is then formulated.

In Section 2.0, a general approach to correlating dissolution kinetics data is discussed and several experimental techniques described. Section 3.0 introduces the concept of rate-limiting steps or regimes. Detailed results of previous investigations are presented within this framework. The fourth and final section outlines a series of screening experiments for the present study of $CaCO_3$ dissolution kinetics.

2.0 GENERAL ASPECTS OF DISSOLUTION KINETICS

As in the previously described precipitation kinetics study (Radian Technical Note 200-014-06) it is convenient to formulate a rate expression for dissolution in forms of measurable process design variables. This is normally written as in Equation 2-1.

$$R = k \cdot M \cdot \emptyset \quad \text{mole liter}^{-1} \ \text{min}^{-1} \qquad (2\text{-}1)$$

R is the dissolution rate of a given substance, k is a rate "constant" which may vary with liquor temperatures, composition, and transport parameters, M is a term dependent on the amount of solid phase present, and $\emptyset$ is some function of the actual and equilibrium concentration of the dissolving species. The typical experimental approach involves measurement of R at known or constant values of M, and/or $\emptyset$. The rate "constant" k is then calculated. Applicable parameters are varied over ranges expected to prevail in a typical process and the measured rates or rate constant correlated for use in large scale design.

The dissolution rate, R, is most commonly determined by chemical analysis of the liquid phase to detect an increase in concentration of the dissolving species. Alternately, the decrease in weight of the solid phase may be measured. The "M" term is usually assumed to correspond to the exposed surface area of the solid phase. This obviously may be difficult to quantify in experiments with suspensions of many fine particles. Ø is nearly always taken to be the difference between the actual and equilibrium concentration of the dissolving species, perhaps raised to some power. In more complex solutions, the driving force needs obviously to be written as a function of ion activation if it is to vanish explicitly at saturation (see Radian Technical Notes 200-403-09 and 200-014-06).

In order to quantify R, M, and Ø, a means of contacting the two phases must be selected. Three categories generally considered are fixed-solid/moving liquid, moving solid/"fixed" liquid (agitated only by the solid itself), and agitated liquid/suspended solid. The first two techniques are generally used in more fundamental studies where it is desirable to have quantitative descriptions of liquid velocity profiles and well defined surfaces for dissolution. Since the present study is intended for direct application to limestone scrubbing process design where agitated tanks will be used, only the third technique will be considered here. Quantitative application of data from flow situations other than an agitated suspension does not appear to be practical, given the present knowledge of phenomena involved.

As in the precipitation study there are at least three choices regarding experimental operation of an agitated vessel. These are as follows:

a. batch liquid-batch solid

b. continuous liquid-batch solid

c. continuous liquid-continuous solid

The first of these is simplest from the operational standpoint but the most complex in terms of data analysis. A characterized batch of seed crystal is introduced to a subsaturated solution and the concentration of the liquor monitored with time. For slow dissolution, grab samples give adequate results. For faster rates, in-situ measurement using ion electrodes or conductivity is required. Calculation of the dissolution rate involves differentiation of the concentration versus time data as well as correction for any significant changes in area of the seed crystals during an experiment. An additional complication can arise if the rate is both particle size and area dependent as happens in some cases (see Section 3.0).

The continuous liquid-batch solid method is very convenient for systems in which the change in the amount, area, and size of seed crystals is negligible during an experiment. Under these conditions, a "steady state" material balance for the liquid phase gives the rate directly without differentiation of a concentration curve.

The third method is the most difficult to achieve experimentally since continuous addition of solids is necessary. It does, however, offer a true steady-state rate regardless of changes in the solid mass, area, and size. The rate is calculated directly from a steady state liquid or solid species balance.

For the present study, method b can be employed for dissolution of $CaCO_3$ in neutral solutions. For higher dissolution rates in acid solution, continuous solids feed may be necessary.

3.0 PREVIOUS WORK

For purposes of discussion, previous studies of dissolution kinetics have been organized according to the rate-limiting step for mass transfer. Possible rate-limiting mechanisms are discussed in Section 3.1. Sections 3.2-3.6 describe the results of previous investigations.

3.1 RATE LIMITING REGIMES FOR DISSOLUTION KINETICS

Qualitatively, the following physical phenomena are involved in dissolution of an electrolyte. First, an ion pair of the dissolving substance must detach from the crystal lattice. Dissociation and hydration may also be involved in this step. The combination of removal of an ion pair and dissociation and hydration of the ions will be termed "surface reaction" in this discussion.

The ions next must diffuse through the liquid boundary layer or film into the bulk solution. This step will be termed diffusion. In addition to these steps, the diffusing ions may react with other ions in solution. For example:

$$CO_3^{=} + H^{+} \rightleftarrows HCO_3^{-} \qquad (3\text{-}1)$$

Such a reaction would change the concentration gradient and thus, the diffusion rate of the diffusing ions. This type of reaction will be termed "bulk reaction".

Since the steps set forth above are in series, any or all of them may contribute significantly to the overall rate. In some cases, if the rate of one step is much less than that of the others, the slow step is said to be rate-limiting. That is, the overall rate cannot proceed faster than the slowest step. More commonly, two or more steps may be of equal magnitude and furthermore, will interact through their individual contribution to the species concentration profile near the solid particle.

Table 3-1 summarizes five major rate-limiting regimes considered in this study. Identifying features of each regime in terms of observable experimental effects are noted.

3.2 SURFACE REACTION LIMITED DISSOLUTION

Referring to Table 3-1, surface reaction limited dissolution is characterized by high activation energies (temperature dependence), little or no effect of particle size and agitation, and significant dependence on crystal type and structure. Several investigators have noted such behavior in previous experimental determinations of dissolution kinetics. Important details of these studies are summarized in Table 3-2.

Nestass and Terjesen, in a study of $CaCO_3$ dissolution in CO_2-saturated water, showed that the dissolution rate was independent of agitation and was sensitive to adsorbed ions (Sc^{+3} in this case). They also estimated a purely diffusion-limited dissolution rate to be considerably higher than the observed rate.

TABLE 3-1 - DISSOLUTION RATE REGIMES

Surface Reaction	Surface Reaction + Diffusion	Diffusion	Diffusion + Liquid Phase Reaction	Liquid Phase Reaction
(Slow surface reaction, fast diffusion)	(Diffusion and surface reaction rates of equal magnitude)	(Fast surface reaction, slow diffusion of ions away from surface)	(Fast surface reaction, slow diffusion affected by reaction of diffusing species in the liquid film)	(Fast surface reaction, fast diffusion)
Major Variable Effects				
Rate constant is independent of agitation and particle size. Activation energy may be high (significant temperature dependence of rate). Rate may be proportional to number of active sites rather than surface area. Limestone type and crystal structure can have a major effect on rate.	Rate constant sensitive to agitation and particle size at high temperature. Less sensitive at lower temperature. Rate constant more sensitive to temperature at high agitation and small particle size. Intermediate activation energy. Rate may be influenced by surface area and number of active sites. Limestone type could be important.	Rate constant sensitive to agitation and particle size. Low activation energy. Limestone type should not be an important variable.	Rate constant sensitive to agitation, particle size, and concentration of reactants in bulk liquid. Low activation energy. Limestone type not important. Possible reacting species affecting the rate are H^+, $SO_3^=$, and $SO_4^=$ (also HSO_3^-, HCO_3^-).	Rate constant independent of agitation, particle size, and crystal structure.
Driving Force Form				
Driving force based on bulk species activities and solubility product (K_{sp})	Driving force based on unknown intermediate value of species activities in liquid film. "Resistances" are additive only if a linear driving force applies to the reaction step as well as the diffusion step.	Driving force is linear with the difference of actual and equilibrium species activities in the bulk solution.	Driving force is linear with species activities.	Driving force involves activities of reacting species in the bulk solution in addition to dissolving species.
Correlation + Scale-up Techniques				
Correlation and scale-up not difficult for a single crystal type. A well-defined driving force function and temperature dependence may be determined in lab.	Correlation and scale-up extremely difficult even for a single limestone type. Laboratory rate constants and driving force functions may not be applied in large vessel unless strictest attention is given to system geometry. Data are needed over entire range of all variables.	Good correlation and scale-up possible over reasonable particle size ranges and for geometrically similar vessels and agitators. Conventional dimensionless groups used to calculate mass transfer coefficient.	Correlation and scale-up more difficult than simple diffusion regime. Rate constant must be correlated with bulk concentration of reactants in addition to other parameters in diffusion regime.	Correlation and scale-up not difficult if only a limited number of reacting species is involved.

TABLE 3-2 - SURFACE REACTION LIMITED DISSOLUTION

Reference	Chemical System	Mechanical System	Range of Variables	Rate Correlation	Other Conclusions
Nestaas and Terjesen NE-032	$CaCO_3$ in H_2O under CO_2 pressure (Inhibited by Sc^{+3} ions)	Not specified. Agitated suspension with CO_2 gas bubbled through	Not specified	Rate = $k(C^*-C)-k'C_{S_c}^{+3}$	Agitation had no effect. Estimated diffusion-limited mass transfer rate was significantly higher than observed rate.
Drehmel	Lime and Limestone in water and H_2SO_3	Trickle funnel and small magnetically stirred beaker. Batch solids dissolution at constant pH	12 solid types. pH 4 to pH 7 solutions 70-110°F temperatures 100-1000μ particles	None given	Interpretation of results must be qualitative since driving force functions were not calculated. 5-6 kcal/mole activation energy for $CaCO_3$ dissolution. Surface area effect less than 1.0 power. Factor of 30 difference in apparent dissolution rate of marl and calcite.
Armstrong and Prosser AR-014	Pure MgO crystals in 1.38 M HCl	Agitated suspension. Batch solid and liquid	1°C, 40°C Large single crystals Also ground crystals with mean particle sizes of 5, 16, 55, 156, and 350 microns	None given	Dissolution proportional to BET surface area which was ~10x external area. Grinding, polishing, and/or cleaning alters the dissolution rate markedly (in addition to surface area effects). Particle size effects due to increase in ratio of deformed surface thickness to total crystal thickness.
Bovington and Jones BO-048	$BaSO_4$ in H_2O	Fixed plate in stirred solution. Batch solid and liquid	10.5°C, 35°C	Rate=$k(C^*-C)^2$	No effect of 50% increase in agitation. High activation energy ~25 kcal/mole.
Campbell and Nancollas CA-065	$SrSO_4$ in H_2O	Agitated 250 ml flask	15μ seed crystals	Rate=$k\,A(C^*-C)^2$	Surface active substances inhibit dissolution rate markedly.
Little and Nancollas LI-033	$PbSO_4$ in H_2O	Not specified	40μ seed crystals	Rate=$k\,A(C^*-C)^2$	Rate inhibited by tetrametaphosphate.

Drehmel studied dissolution rates of 12 naturally occurring limestones and dolomites using a constant pH titration technique. Although the measured activation energy for limestone dissolution was comparable to that expected for a diffusion limited mechanism (5-6 kcal/mole), dissolution rates varied by as much as thirty times with different limestone types. This behavior indicates a strong dependence on a surface reaction step.

Dependence of dissolution rate on surface effects was also demonstrated by Armstrong and Prosser. In work with MgO crystals dissolved in 1.38M HCl, grinding, polishing and/or cleaving altered dissolution rates of single crystals markedly in excess of effects accounted for by surface area changes. They postulate that dissolution is related to lattice dislocations on the crystal surface in a manner similar to precipitation processes. Studies with different particle sizes produced a threefold increase in dissolution rate per unit area as crystals were ground from 350μ to 5μ mean particle size fractions. This rate increase in excess of the area increase was attributed to an increase in the number of dislocations or active sites for dissolution.

These three studies have in common alkaline solids dissolving in acid solutions. Under these circumstances, the liquid film diffusion resistance could be unusually low due to liquid phase reaction of diffusing species. The observation that dissolution rates are surface reaction limited for this situation is quite reasonable. This behavior cannot be generalized to neutral or alkaline solutions, however, since diffusion and surface reaction resistances may then be of similar magnitudes.

Nancollas and several coworkers have studied the dissolution rates in water of slightly soluble sulfates including $BaSO_4$, $SrSO_4$, and $PbSO_4$. All of these investigations led to a driving force term of the form

$$\phi = (a^* - a)^2 \qquad (3\text{-}2)$$

where a* is the equilibrium activity of the dissolving species and a is the activity in the bulk solution. This form is probably not representative of a diffusion limited rate mechanism. The dissolution rates were also found to be significantly inhibited by trace amounts of surface active additives such as tetrametaphosphate. In the $BaSO_4$ investigation, a 50% increase in stirring rate had no effect. Also, an activation energy of 25 kcal/mole was observed. This work shows that a surface reaction can limit dissolution even when diffusion is not aided by reaction in the liquid film.

In general, it is quite possible that the rate limiting mechanism for limestone dissolution may change as the acidity of the solvent solution increases or decreases. This will be a consequence of reaction of H^+ with the diffusing $CO_3^=$ or OH^- ions in the liquid film (see Section 3.5).

3.3 SURFACE REACTION AND DIFFUSION LIMITED DISSOLUTION

The postulated mechanism for dissolution includes a number of steps in series which all depend on concentration profiles of the dissolving species. These conditions can result in intermediate regimes where both diffusion and reaction rates contribute significantly to the observed overall rate. Experimental effects characteristic of intermediate rate-limiting regimes have been noted in several previous studies of dissolution kinetics. These are summarized in Table 3-3.

TABLE 3-3 - SURFACE REACTION AND DIFFUSION-LIMITED DISSOLUTION

Reference	Chemical System	Mechanical System	Range of Variables	Rate Correlation	Other Conclusions
MacDonald and Owen MA-142	MgO in H_2SO_4	Pellets imbedded in rotating disc	4°C, 25°C 100-1000RPM (laminar flow regime)	None given explicitly	Dissolution is first order with respect to H^+ (Inversely proportional to OH^-). Rate constant is a function of speed of rotating disc. Rate constant versus speed of rotation plot is assymptotic at high level. The rate dependence on rotation is greater at 25°C than at 4°C. Fast hydration followed by slow dissolution is postulated.
Erga and Terjesen ER-007	$CaCO_3$ in CO_2-saturated water	10 liter agitated vessel. Batch solid and liquid	300-400μ particles, .95, .66, .39, .135 atm CO_2 partial pressure, 280-555 RPM	Rate=k (C^*-C) where C^* and C are bicarbonate concentrations	Rate inhibited by Cu^{++} ions. $k \alpha (RPM)^{.3}$
Lin and Nancollas LI-031	$CaSO_4 \cdot 2H_2O$ in H_2O	250 ml stirred flask. Batch solid and liquid.	10°-30°C 150, 300, 600 RPM	Rate=k $A(C^*-C)$ with $k \alpha (RPM)^{.8}$ and $k \alpha \exp[10,000/RT]$	The dissolution rate of $CaSO_4$ is considerably faster than other sulfate studied (see 3.2). An activation energy of 10 kcal/mole was observed.

The paper by MacDonald and Owen presents an excellent discussion of series rate steps and experimental observations indicating both surface reaction and diffusion resistances. The temperature/agitation interaction observed in this study of MgO dissolution is typical of the combined rate limiting mechanism. The experimental dissolution rates were influenced by speed of rotation of the MgO pellets, but less so than predicted by mass transfer theory. Furthermore, the effect of rotation was less at a lower temperature as the reaction step became more significant. These investigators also note that the rate of increase of dissolution with agitation becomes small at high levels of rotation as the diffusion resistance becomes negligible with respect to the reaction resistance. The rate increase with temperature corresponded to an activation energy ranging from 4.5 kcal/mole at low rotation speeds to 6 kcal/mole at high speeds.

Erga and Terjesen studied $CaCO_3$ dissolution rates in CO_2-saturated water. They found the rate was inhibited by trace qualities of copper ions, indicating significant surface reaction effects. The rate was dependent on agitation, but to a lesser extent than expected for a diffusion-limited mechanism.

Liu and Nancollas observed similar behavior in dissolution experiments with $CaSO_4 \cdot 2H_2O$ in water. Their experimental dissolution rates were proportional to the agitator speed to the .5 power. The observed activation energy was 10 kcal/mole indicating some contribution from a resistance other than diffusion.

3.4 DIFFUSION-LIMITED DISSOLUTION

The bulk of reported investigations of dissolution rates in agitated vessels fall into the diffusion limited category. Many attempts have been made to develop general correlations of diffusion-limited dissolution rate constants with vessel and agitator design parameters. Historically, most dissolution processes have been assumed to be diffusion rate limited. Consequently, the absence of contributions from surface or bulk reaction has not been experimentally verified in most cases. This point must be kept in mind when reviewing available information. Details of several studies appear in Table 3-4 in chronological order.

The types of correlations proposed for prediction of diffusion-limited solid-liquid mass transfer can be categorized as follows:

a. Frössling correlations based on particle Reynolds number

$$kD_p/D = 2 + A\, N_{Re}^{B}\, (\nu/D)^{c} \qquad (3\text{-}3)$$

where D_p is the particle diameter and $N_{Re} = D_p U_T/\nu$. Here, U_T is the so-called slip velocity or terminal velocity of the particle in the fluid.

b. Gilliand-Sherwood correlations of the form

$$k\, d/D = A\, N_{Re}^{B}\, (\nu/D)^{c} \qquad (3\text{-}4)$$

TABLE 3-4 - DIFFUSION-LIMITED DISSOLUTION

Reference	Chemical System	Mechanical System	Range of Variables	Rate Correlation	Other Conclusions
Hixon and Baum HI-011	Benzoic acid, rock salt, and $BaCl_2$ in water. Naphthalene in methanol	4-blade, 45° pitch agitators 15, 21, 26, 36, 46, 61 cm. vessels similar geometry maintained height = diameter	100-500 RPM Room temperature. Large particle regime.	Above $N_{Re} = 6.7\times10^4$ $Kd/D = .16\left(\frac{nd^2\rho}{\mu}\right)^{.62}$ $(\mu/\rho D)^{.5}$ Below $N_{Re} = 6.7\times10^4$ $Kd/D = 2.7\times10^{-5}$ $(nd^2\rho/\mu)^{1.4}(\mu/\rho D)^{.5}$ where K=mass transfer coefficient d=tank diameter D=diffusivity of dissolving species n=stirrer RPM ρ=fluid density μ=fluid viscosity	Two different rate regimes probably due to incomplete particle suspension at low N_{Re} Temperature effects not checked.
Mack and Marriner MA-146	Benzoic acid .0019M NaOH	9.7" and 16" diameter x 24" high baffled tanks Batch liquid and solid.	57°F-82°F 2, 4, 6-blade agitators with 3 to 11" blades 250-fold range of particle surface area, 92-1550 RPM .0083 - .82 H.P. Large particle regime (7mm+)	$d/\theta = (H/d)^{.18} = f$ $[(Pg/n^3L^5\rho)^{.44}nL^2]$ where H=liquid height θ=neutralization time P=power L=impeller diameter	No particle size effect. Baffle size and type not significant. (Only presence or absence had effect.) Temperature effects not checked.
Humphrey and VanNess HU-006	$Na_2S_2O_3\cdot5H_2O$ in H_2O	6-gallon baffled tank 12" diameter x 12" high Propeller and turbine type agitators. Steady state continuous flow of solids and liquids	200-600 RPM with turbine 400-1300 RPM with propeller Large particle regime (.75-1.5 mm)	$Kd/D = a(\mu/\rho D)^{.5}$ $(nd^2\rho/\mu)^b$ a=.13 for propeller =.0032 for turbine b=.58 for propeller =.87 for turbine	No particle size effect. Temperature effects not considered.
Mattern, et.al. MA-180	NaCl in brine	1.3 liter vessel 4½" diameter x 5½" high (fully baffled) 1½" marine propeller	20-30 mesh NaCl (3 fractions) 1000-1500 RPM	Rate = k A(C*-C) No correlation for k given	100u or smaller particles were nearly perfectly mixed. No effect of impeller speed for 1000 RPM and above. No particle size effect for large particles. Equations given for various CSTR configurations. Temperature effects not considered.

TABLE 3-4 - DIFFUSION-LIMITED DISSOLUTION (cont.)

Reference	Chemical System	Mechanical System	Range of Variables	Rate Correlation	Other Conclusions
Barker and Treybal BA-125	Boric acid, benzoic acid, and rock salt in water and sucrose solutions	6, 12, 18, 30" baffled vessels 2, 3, 4, 6, 9, 12" diameter 6-blade turbines. Batch liquid and solids.	Large particle regime (.5-1.5 mm) 500-1400 RPM for small turbine 200-700 for medium 140 for large Density difference .06-.99 g/cm³ N_{Sc}=1140-62000 for benzoic acid =735-55000 for boric acid	Turbine N_{Re} adequate to correlate k for a single vessel, but not generally $N_{Sh}=.052N_{Re}^{.83}N_{Sc}^{.5}$ where $N_{Re}=nL^2\rho/\mu$ Power/unit volume not adequate to correlate data	No particle size effect. No effect of density difference. Diffusivity not significant. No effect of turbine/tank diameter ratio. Baffles increase k significantly. No effect of weight percent solids in reactor. Temperature effects not considered. Power/unit volume not adequate to correlate data.
Calderbank and Moo-Young CA-066	CO_2 in H_2O and glycol, O_2 in H_2O and brine, H_2 in wax, Resin beads in H_2O	Dispersed bubbles in agitated vessel	Wide range of diffusivities and viscosities, 100μ to 8 mm bubbles. Other variable ranges not specified .	$kN_{Sc}^{2/3}=.13[P/V\mu/\rho^2]^{1/4}$ (with ~66% std. deviation) Power required to suspend particles correlated by $P/V=const(g\Delta\rho)^{1.38}$ $\mu^{.3}D_p^{1/8}(wt\%)^{.4}/\rho^{.38}$	Impeller N_{Re} type correlations are consistent with this development, but require similar geometry for extrapolation. After particles are suspended, little is gained from additional power.
Marangozis and Johnson MA-149	Benzoic acid in H_2O, O-salicylic acid in H_2O, benzoic acid in glycerol solutions	Baffled agitated vessel 6" diameter x 12" high. Continuous liquid, batch solid (fixed in vessel bottom). 3" diameter 6-blade turbine.	N_{Re} $5x10^5 - 10^8$ 25.0°C	$kd/D = .402(N_{Sc})(N_{Re})^{.48}$ (turbine Reynolds no.) Transition effect noted at N_{Re} = 60,000	Temperature not considered.
Marangozis and Johnson MA-147	Review of previous data			$kd/D = aN_{Sc}^{b}N_{Re}^{c}$ where $N_{Re} = nL^2\rho/\mu$	Temperature not considered. Large deviations from correlation. Unbaffled dissolution rates 2.5 times baffled rate.
Harriott HA-111	Benzoic acid, $PbSO_4$, ion exchange beads, and boric acid in water and polymer solutions.	4" flask, 8 and 21" tanks. 1½, 2, 3, 4, and 7" 6-bladed turbines.	Wide range of variables .07 - 122 HP/1000 gal, 130 - 1500 RPM for small vessel, 85 - 1500 for intermediate 200 RPM for large tank, 15 μ to 1000 μ particle size.	No satisfactory correlation for all data. For Dp > 100 μ, $k\alpha n^{.9}$. For Dp = 15 μ, $k\alpha n^{.8}$. For Dp < 200 μ, $k\alpha Dp^{-.5\rightarrow-1.0}$. For $\Delta\rho$ > .4 g/cm³, $k\alpha\Delta\rho^{.5\rightarrow.6}$ (cont.)	Effect of baffles on rate depends on degree of particle suspension. Temperature not considered. No particle size effect for Dp > 200 μ. Use of power/volume or turbine N_{Re} is not meaningful in general. (cont.)

TABLE 3-4 - DIFFUSION-LIMITED DISSOLUTION (cont.)

Reference	Chemical System	Mechanical System	Range of Variables	Rate Correlations	Other Conclusions
Harriott HA-111 (cont.)				Best general correlation uses slip velocity theory followed by corrections for Dp, n, and L/d.	Power/volume may be adequate if similar geometry is maintained. No effect of wt.% solids for large particles.
Miller MI-059	Review of previous work			No satisfactory general correlation has been formulated.	Suggests the use of an effective turbulent diffusivity rather than the usual molecular value would improve results.
Middleman MI-066	Discussion of Harriott's data.			Suggests use of Kolmogoroff theory of isotropic turbulence to establish slip velocity for use in Frössling-type correlation. $N_{Sh} = 2 + .6N_{Re}^{\frac{1}{2}}N_{Sc}^{1/3}$ This technique relates the particle Reynolds number to the impeller Reynolds number.	
Miller MI-056	Benzoic acid in H_2O	1, 10, 100 gallon baffled agitated vessels with fixed pellets of BzOH. 4, 8, 18" 4-blade paddles in 6, 12, and 27" vessels. Batch solid, continuous liquid. Geometric similarity maintained.	Impeller N_{Re} 27,270 - 637,830 P/V .04 - 16.6HP/1000 gal. 170-450 RPM in small vessel. 110-300 in intermediate. 20-170 in large vessel. 1/8, 1/4, 1/2, 1⅛" pellets.	Frössling equation used. $N_{Sh} = 2 + 1.1N_{Re}^{.8}N_{Sc}^{.33}$ Large standard deviation in data fit to this correlation.	No comments on estimation of slip velocity for suspended particles. If particle size remains the same with scale-up, fixed impeller tip speed is good criterion.
Nienow NI-012	K_2SO_4, NH_4Cl, alum, NaCl, KCl all in water solution	4 and 6-blade turbines. 12 and 14 cm-baffled vessels. Batch solid and liquid.	3-fold density range, 5-fold diffusivity, 200 μ - 10 mm particle size. Several different impeller positions. 100-2000 RPM.	Frössling equation used with slip velocity calculation modified for particle size effects. $k \alpha n^{.8}$ for low impeller position $k \alpha n^{1.0}$ for high impeller position $k \alpha \text{ Power}^{.18}$ after particles are suspended Actual k's will be 10-50% greater than predicted k's.	Impeller position has little effect at high enough RPM to suspend all particles. Small particles yield predicted coefficients close to actual values. Power/volume is not an economical method to increase k after particles are suspended.

TABLE 3-4 - DIFFUSION-LIMITED DISSOLUTION (cont.)

Reference	Chemical System	Mechanical System	Range of Variables	Rate Correlations	Other Conclusions
Brian, et al. BR-083	Pivalic acid in H_2O	Stirred flask 12 cm diameter x 11 cm high. Fully baffled 6 cm 3-blade marine propeller, 5 cm 4-blade turbine agitator. Batch liquid and solid.	100-400 RPM Power/$n^3L^5\rho$ = .42 for marine propeller = 11.1 for turbine Large particles 1.5-3 mm.	$N_{Sh} = f\left(\frac{P/VD_p^4\rho^2}{\mu^3}, N_{Sc}\right)$	Data are very scattered. Negligible effect of $\Delta\rho$ for $\Delta\rho < 25\%$. No particle size effect for large particles.
Miller MI-020	Benzoic acid in H_2O	1, 10, 100 gallon tanks, 4-blade turbines. Geometric similarity maintained. Batch liquid and solid.	Large particles (also uses Harriott's small particle data): 0.5 - 19 HP/1000 gal. 170-490 small tank RPM 100-290 intermediate 25-170 large	For large particle flow regime, the Frössling equation is used to get k_{min}. Then $k/k_{min} = .027(RPM)^{.8}$. For small particle regime . $N_{Sh} = 2$ and $D(\text{effective}) = D \times 3.08\left(\frac{P}{V}\right)^{.18}$.	For Dp < 200 μ, radial diffusion is dominant mechanism. Power input/volume is not adequate for scale-up.

where k is the mass transfer coefficient,
d a characteristic length for the system,
D the diffusivity of the dissolving species,
ν the kinematic viscosity of the liquid,
and N_{Re} a system Reynolds number. N_{Re} may be based on tank dimensions: $N_{Re} = nd^2/\nu$ (n = RPM, d = tank diameter), or impeller dimension: $N_{Re} = nL^2/\nu$ (L = impeller diameter).

c. Power input correlations of the form

$$k = f\,(\text{Power/Volume} \times \mu/\rho^2)$$

Early investigators generally used the Gilliand-Sherwood form. The studies of Hixon and coworkers, Humphrey and Van Ness, and Barker and Treybal are typical of this approach. Characteristic observations of variable responses include no effects due to particle size, Reynolds number exponents ranging from .5 to .9, Schmidt number exponents of .3 to .5, and significant differences between baffled and unbaffled vessels, but no effect of baffle type or size.

Harriott and other proponents of the slip velocity/Frössling equation approach have pointed out the fundamental difficulty of the Gilliand-Sherwood correlation in that it completely ignores the fact that qualitatively, the mass transfer rate must depend on the velocity profile near the particle itself. The use of a Reynolds number based on propeller speed and tank or propeller diameter is obviously not theoretically justified and consequently cannot be safely extrapolated. This has been demonstrated experimentally. Correlations based on impeller Reynolds number are not valid over varying tank dimensions and those based on tank dimensions and tank Reynolds number vary with impeller dimensions.

The apparent particle size independence of the Gilliand-Sherwood correlation has also proved incorrect. For sufficiently small particles, ($D_p < 200$ microns), the mass transfer rate is a strong function of particle size.

The slip velocity approach based on the Frössling equation is more satisfying theoretically, but also suffers several practical limitations. This correlation is given by

$$kD_p/D = 2 + A\ (D_p U_T \rho/\mu)^{.5}\ \ (\nu/D)^{.33} \qquad (3\text{-}6)$$

The first term on the right hand side represents the contribution to the rate from molecular diffusion and the second from forced convection. In the large particle regime, the second term dominates. In the small particle regime, the slip velocity U_T approaches zero and the first term dominates.

The terminal or slip velocity of the particle must be estimated in order to use Equation 3-6. Normally, this may be done using conventional drag coefficients for spheres, but the resulting values are usually low and yield a conservative value for k. The discrepancies arise from the fact that the turbulent eddy size in agitated vessels may be of the same order of magnitude as the particle diameters.

For small or very light particles, the slip velocity approaches zero and the molecular diffusion term determines the rate. Again, difficulty is encountered in this case. The actual or effective diffusivity generally is greater than the stagnant molecular diffusivity because of transport by turbulent eddies. Predicted mass transfer coefficients fall lower than actual values as a result.

Hariott and Miller have both proposed empirical corrections to the basic slip velocity theory to account for these discrepancies. The generality of these schemes is questionable, of course.

The third major approach to prediction of diffusion limited mass transfer is based on the Kolmogoroff theory of isotropic turbulence. Qualitative reasoning regarding the mechanism of energy dissipation in agitated vessels leads to the conclusion that the velocity field "seen" by suspended particles should be primarily a function of power input per unit volume. A dimensionless group involving the agitator power input and the viscosity and density of the solution is used to correlate k. The power/unit volume for a given agitator and speed of rotation is a function of system geometry. Thus, this approach requires geometric similarity to be maintained.

Papers by Barker and Treybal, Calderbank and Moo-Young, Harriott, Middleman, and Nienow (see Table 3-4) discuss the power input approach to vessel scale-up. In general, this correlation technique appears to be less successful than the slip velocity approach.

Summarizing previous work on diffusion limited dissolution, important variables that must be considered in this rate limiting regime are as follows:

- Agitator design, speed of rotation, and location.

- Tank geometry and baffling.
- Fluid transport properties.
- Particle size and density.
- Minimum agitation necessary to suspend particles.

Some important generalizations that appear throughout the literature are as follows:

- Particle size effects are important for small particles only ($D_p < 200$ microns).
- Power input increases the mass transfer rate significantly only in the region where full particle suspension has not been achieved. Above this level, the rate varies with power to the .2 or less exponent.
- Particle-liquid density differences are significant at levels higher than 25%.
- The presence or absence of baffles affects the rate, but the type of baffling does not.
- The mass transfer rate is independent of slurry density for large particles.

- Maintenance of geometric similarity is necessary for reliable design and scale-up.

3.5 DIFFUSION WITH CHEMICAL REACTION IN THE LIQUID PHASE

In a diffusion-limited mass transfer situation, any variable that changes the activity gradient of the diffusing species will change the overall rate. Thus, removal of diffusing ions from solution by chemical reaction will increase the rate by increasing the activity gradient. This mechanism may prove to be very important in lime or limestone dissolution in scrubbing liquors.

Since diffusion processes are greatly complicated by chemical reaction, relatively few experimental studies have characterized this rate limiting regime. Applicable studies are summarized in Table 3-5.

The usual approach to correlation of mass transfer coefficients when liquid phase chemical reaction is significant is to examine the ratio of k with diffusion and reaction to k with diffusion only as a function of the concentration of reactant (s) in the liquid phase. For the simplest case of a rapid irreversible reaction between a single dissolving substance A and a liquid phase reactant B, the film theory of dissolution leads to

$$k/k_0 = 1 + D_B C_B / D_A C_{As} \tag{3-7}$$

Other more complex functional relationships result with reversible reactions and reactions involving several species. Ionic reactions make the problem more difficult because of charge interaction between the diffusing species.

TABLE 3-5 - DISSOLUTION LIMITED BY DIFFUSION AND LIQUID PHASE REACTION

Reference	Chemical System	Mechanical System	Range of Variables	Rate Correlations	Other Conclusions
Sherwood and Ryan SH-073	Bonzoic acid in water and NaOH so solution (2nd order fast irreversible reaction).	Rotating cylinder 30 mm diameter in a 10 cm diameter, 1.5 liter vessel.	17°C, 25°C, 33°C N_{Re} = 136 - 103,400	$\frac{k}{k_0}$ α NaOH concentration in bulk solution. Film Theory: $A+B \xrightarrow{Fast} AB$ $\frac{k_A}{k_{A0}} = 1 + \frac{D_B C_{B0}}{D_A C_{Ai}}$ Corrected for ion Diffusion: $\frac{k_A}{k_{A0}} = 1 + \frac{2RT\lambda}{D_A F^2} \times \left\{\sqrt{1 + \frac{C_{B0}}{C_{AB0}}\left(\frac{\lambda_A}{\lambda_B} - 1\right)} + 1\right\}^{-1} \frac{C_{B0}}{C_{Ai}}$ where: λ = ionic conductance F = Faraday's constant C_0 = concentration in bulk solution C_i = concentration at partical surface.	
Marangozis and Johnson MA-149	Benzoic acid and O-salicylic acid in NaOH and KOH solutions.	6" diameter x 12" high agitated vessel with 3" 6-blade turbine. Organic acid cast in ring on bottom.		Boundary layer theory with ion diffusion effects. $\frac{k_A}{k_{A0}} = \left(\frac{N_{Sc_B}}{N_{Sc_A}}\right)^{1/3} + \left(\frac{N_{Sc_A}}{N_{Sc_B}}\right)^{2/3} \frac{C_B}{C_{Ai}}$ Ion diffusivities used in N_{Sc} (see Sherwood and Wei).	
Vermilyea VE-013	MgO, $Mg(OH)_2$ in KCl and $KClO_4$ solutions.	Not specified.	10-30 μ particles, slow agitation, pH 3 to pH 10.	Rate mechanism apparently changes in different pH ranges.	Very poor reproducibility of results.

Sherwood and Ryan conducted dissolution experiments with benzoic acid in water and dilute NaOH solutions. After establishing a correlation for the mass transfer coefficient, k_o, without reaction, NaOH solutions were used to establish a correlation for mass transfer with reaction. Results could be adequately correlated using the film theory corrected for ion diffusion effects. Boundary layer theory predicted a slightly lower enhancement factor (k/k_o). The experimental range of k/k_o varied from 1.6 to more than 30 as the ratio of NaOH to the saturated benzoic acid concentration increased from .3 to 20. Use of the film theory with molecular diffusivities rather than individual ion values leads to errors greater than 50 percent. The actual value of the enhancement factor is considerably greater than that predicted using molecular diffusivities especially where the reacting ions diffuse faster than the dissolving ions.

Marangozis and Johnson studied dissolution of benzoic acid in NaOH and KOH and O-salicylic acid in NaOH. Their results agreed well with enhancement factors predicted by boundary layer theory corrected for ion diffusion effects. Experimental k/k_o ratios ranged from 2 to 15 as the ratio of NaOH to dissolving species concentration was increased from .4 to about 4.

Considering the magnitude of these effects, if the reaction of H^+ and $CO_3^=$ affects the rate of $CaCO_3$ dissolution, it would do so even at relatively neutral levels of pH. This is a consequence of very low equilibrium levels of $CO_3^=$ in limestone scrubbing solutions. That is, the concentration of H^+ is of the same order of magnitude as that of $CO_3^=$ even at a pH of about 7.

An investigation by Vermilyea with MgO and $Mg(OH)_2$ showed an apparent change of mechanism from simple diffusion to diffusion plus reaction limited regimes as the pH was varied. The experimental results of this study were not very reproducible, but serve to illustrate the possibility of a change in rate limiting mechanism over a range of experimental conditions.

3.6 LIQUID PHASE REACTION LIMITED DISSOLUTION

Although no previous experimental studies of dissolution limited by liquid phase reactions were found, this rate limiting regime could be encountered in limestone scrubbing processes. Conceptually, if limestone dissolution rates were much faster than $CaSO_3 \cdot \frac{1}{2}H_2O$ and $CaSO_4 \cdot 2H_2O$ precipitation rates, the rate of dissolution of limestone could be limited by the rate of precipitation. The possibility of this situation can perhaps be estimated given adequate rate data for limestone dissolution.

4.0 SCREENING EXPERIMENTS

Because of the possible complexity of the limestone dissolution rate form and the fact that it may change with processing conditions, it is desirable from an experimental standpoint to establish ranges of rate limiting regimes before attempting rate correlations. A set of screening experiments for this purpose has been devised based on major variable effects noted in previous studies.

Table 4-1 summarizes conditions for these initial experiments. The sequence starts with dissolution in water at high temperature. Under these experimental conditions, surface reaction is favored over diffusion. If no agitation effect is

TABLE 4-1 - LIMESTONE DISSOLUTION SCREENING EXPERIMENTS

	High Temperature (50°C)	Low Temperature (25°C)
Water (CO_2 free)	1. High Agitation	3. High Agitation
	2. Low Agitation (If significant, check 25°C level.)	4. Low Agitation
Acid (pH 5)	5. High Agitation	7. High Agitation
	6. Low Agitation (If significant, check 25°C level.)	8. Low Agitation

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NOTE: A set of eight experiments will be performed with each of two limestone types.

noted at this level, the dissolution rate will probably be surface reaction limited for most process conditions. If agitation is significant, two more runs in water at 25° will be made. At this lower temperature, the surface reaction will be slower. A similar agitation effect at this temperature would indicate little or no contribution from the surface reaction rate. A decreased agitation effect would point to a combined surface reaction/diffusion rate limiting mechanism for the neutral liquor environment.

Diffusion rates should be greatly increased for dissolution of $CaCO_3$ in acid solution. Experiments 5 and 6 are expected to show a decreased dependence on agitation and an increased surface reaction contribution to the overall rate. Experiments 7 and 8 represent conditions where the ratio of diffusion rate to surface reaction rate should reach an upper bound for normal process conditions.

This series of eight experiments should be conducted with at least two limestone types so that possible differences in surface reaction rates between crystal types can be detected. Particle size effects on rate limiting regimes may also be important.

The results of these screening experiments will provide a basis for additional runs to correlate the dissolution rate with important parameters.

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10.3 APPENDIX C

TRIP REPORTS OF SHAWNEE ANALYTICAL SUPPORT

5 January 1973 (Revised for Final Report)

MEMORANDUM

TO: F. S. LaGrone

FROM: C. T. Shelton

RE: Trip Report

From December 27 through December 29, I visited the Shawnee Steam Plant at Paducah, Kentucky at the request of Joe Barkley of TVA. He wanted the following changes made to the Laboratory Analysis System software:

1) The total sulfate calculation needed to be recorrected. Shawnee personnel thought it was wrong at first and Mike McAnally changed it, but now they decided it was ok originally.

2) Bechtel personnel feel that the weight percent solids in the slurry data is not getting onto the data tape.

3) Shawnee personnel wanted the ability to print out multiple copies of the final report using only one command.

4) Shawnee personnel wanted about 20 default values put into the programs for values that were never changed on the card inputs. This would cut down greatly the number of variables input via cards on some analyses.

When I got to Paducah, Mickey Martin, one of the lab technician shift supervisors, had two more changes:

1) They wanted the sample point number printed in addition to the sample ID and run number in the LISTS system command.

2) The system indicated that not all analyses had been done when they had been.

I made the following changes to the system:

1) I recorrected the sulfate calculation to its original form in FRPRT.

2) I checked to ensure that data from cards for weight % solids actually got onto the disk in the correct locations in the data packet. I then dumped a data packet to mag tape, deleted it from disk, and read it back in. The data for weight % solids were still in the right places.

Evidently, Bechtel personnel are looking in the wrong places on the data tape. I will have Linda Parker (who wrote the tape dump program) call Bechtel to get this straightened out.

3) I changed the final report program, FMAIN, to print up to 99 copies of the final report.

4) I put in all the default values they had requested, still leaving the option of putting values on the cards instead of using the default values.

5) I changed the LISTS system command to print sample point numbers.

6) The message that all analyses were not complete came from the fact that an extra X-ray analysis was done that hadn't been scheduled. I corrected FRPRT and DPSTS to check to see that the analyses scheduled had been done.

7) I changed the DUMPT command to dump data packets to mag tape so that all the data packets could be dumped using one command.

8) I cleaned up the NXSAM command. It was overflowing a format and printing S1**X for sample ID's for ID's greater than 100.

9) I cleaned up the LSTDP command. In creating a data packet, the operator ID section of the data packet was being used to store some other data. This caused a format overflow in LSTDP when operator ID's were printed (*1).

10) I added a new system command, READK to read sample analysis data card images from the keyboard of the teletype or CRT. I emphasized that this was only to be used in case the card reader was broken or for corrections.

I explained all these changes to Joe Barkley, Mickey Martin, and Bob Bell, another shift supervisor. They all seemed to be pleased and said that these changes would help greatly in using the system.

A Data General field service man came by the plant one day to check on the equipment. He was impressed that it was as clean as it was. I noted that the card reader and Beehive CRT were occasionally giving problems.

Distribution: DMC, PSL, MAM, LMP, KS, DMO

15 February 1973 (Revised for Final Report)

MEMORANDUM

TO: F. Scott LaGrone

FROM: C. T. Shelton

SUBJECT: Trip Report, Shawnee Steam Plant, 15 January 1973

Joe Barkley requested that I come to Paducah again. They were having trouble with the X-ray calibration, the aqueous CO_2 calculations, and the line printer. They also wanted several default values put into the program. I suggested a way to take care of the calibration problem, but they could not seem to get it to work. I also suggested that since the aqueous CO_2 program had been working and just quit working, the wrong tape with an old version had been loaded, but Joe felt sure it hadn't been. From Joe's description of the line printer problem, I was fairly certain that there was a hardware problem either in the interface or in the printer itself.

I arrived in Paducah Monday afternoon, January 15, and by that evening had fixed the X-ray problem, determined that the aqueous CO_2 was correct, isolated the line printer problem to the printer itself, and put in all the default values requested. The graveyard shift then set about to try out the changes. All of the changes worked.

Joe Barkley wanted two new computation schemes added to the system. I added a new command to the system, DUSTA, to implement dust analysis calculations. I also added a system command, WETSO, to make wet SO_2 analysis calculations that Joe requested. Shawnee personnel tried out the new commands and seemed pleased that the dust analysis and wet SO_2 calculations process would be greatly speeded up.

The Data General service man came Wednesday to fix the line printer. When that is fixed, the whole system will be in good shape, including the CRT. Apparently, there are still a few problems with the card reader so I asked Gerald Wood to get Nathan Burris, the instrument mechanic, to tune it up.

The additions to the system included putting the results into the data packet so they would be dumped to mag tape with the rest of the data for Bechtel. I will contact John Jacobs at Bechtel to tell him what and where these data are.

Linda Parker and I finally determined that the data for weight % solids that Bechtel could not find on the tape actually had been there all the time, but that Bechtel had been having difficulty interpreting them. Linda and I interpreted it for them so that Bechtel can now process these data.

Distribution: PSL, KS, MAM, LMP, JLP, DMO

New default values have been added for the following station codes and variables:

Sta. Code		
11-15	U_i instrument readings	Average of U_i can be put in for U_i - commas for U_2 & U_3
16	C_s conc of standard soln	4.0
16	U_i instrument readings	Average of U_i's for U_1, commas for U_2 & U_3
17	C_s conc of standard soln	0.4
17	U_i instrument readings	Average of U_i's for U_1, commas for U_2 & U_3
18-22	U_i instrument readings	Average of U_i's for U_1, commas for U_2 & U_3
25	F wt of fixing soln	0.0
26	W_1 wt of container	0.0
	W_2 wt of container + sample	0.05
28	W_1 wt of container	0.0
	W_2 wt of sample + container	0.1

DUSTA

This system command implements the dust analysis computations. The system responds to the command by typing "TYPE IN SAMPLE ID". To terminate the command, type in an up-arrow (↑) in response to this question, otherwise, type the sample identification, for example, SO12X. If the sample ID is incorrect, a question mark is typed out and the question is repeated. "TCA(1), HF(2), OR VENT(3)?" A 1, 2, or 3 followed by a carriage return should be typed in. "INLET (1) OR OUTLET(2)?" is asked next. A 1 or 2 should be typed in. The next question is "NO. OF SAMPLES=". A carriage return may be typed in so that the default value of 12 will be used. Otherwise, the number of samples followed by a decimal point should be typed in followed by a carriage return, e.g., NO. OF SAMPLES = 6.↲ Next the system asks for the barometric pressure at the orifice meter. "PBAR=". The pressure in inches of mercury should be typed in followed by a carriage return. The system asks for the total amount of particulate matter collected: "MN=". This amount in milligrams should be typed in followed by a carriage return. The volume of gas sample through the meter will be asked for: "VM(1)=". The number in parentheses is the sample number. The volume in cubic feet should be typed in followed by a carriage return. Next the average dry gas temperature is requested: "TM(1)=". The temperature in degrees Farenheit should be typed in followed by a carriage return. Next the pressure drop across the orifice meter is asked for: "DH(1)=". The ΔH in inches of water should be typed in followed by a carriage return. VM(2) is asked for next and so on until VM, TM, and DH are typed in for all samples. The grain loading in grains/scf is then typed out: "CS = 10.5678 GR/SCF".

This data is put into the data packet in location XDTA (474) and is printed on the final report.

NOTE: All input numbers must contain a decimal point. No checking is done on the ranges of the input or calculated variables.

WETSO

This system command implements the wet SO_2 calculations. The system responds to the command by typing: "TYPE IN SAMPLE ID". To terminate the command, type in an up-arrow (↑), otherwise, type in a sample identification. If the sample ID is incorrect, a question mark is typed out. The system asks for the scrubber type: "TCA(1), HF(2), or VENT(3)?" A 1, 2, or 3 should be typed in. Then the system asks "INLET(1) OR OUTLET(2)?" A 1 or 2 should be typed in. The control room reading is asked for: "CONTROL ROOM SO_2=". The control room reading in ppm with a decimal point should be typed in followed by a carriage return. Next the time is requested: "TIME=". The time followed by a decimal point should be typed in. The volume should be typed in followed by a carriage return after the volume is asked for: "V=". Next the temperature is requested: "T=". The temperature in degrees Centigrade should be typed followed by a carriage return. The system then asks for the number of milliliters of basic solution used: "ML=". This amount followed by a carriage return should be typed in. Then the normality of the basic solution is asked for: "N=". The normality should be typed in followed by a carriage return. The system then prints out the SO_2 in ppm. "SO_2 = 1234. PPM". The system then asks for another sample ID.

NOTE: All input data should contain a decimal point. No checks are made of the ranges of the input variables. The SO_2 ppm is stored in the data packet in XDTA(475) and is printed on the final report.

Operational Changes 1/17/73

1. Default values were added for station codes 11-15,16,17, 18-22,25,26, and 28.

2. System commands were added to implement dust analysis (DUSTA) and wet SO_2 calculations (WETSO).

NEW VALUES ADDED TO DATA PACKET AND MAG TAPE

	Value	Type Variable	Data Packet Word	Mag Tape Byte
1.	Time SO_2 reading was made	Integer	56	217-220
2.	Dust-scrubber, inlet/outlet flags	Integer	57	221-224
3.	SO_2-scrubber, inlet/outlet flags	Integer	58	225-228
4.	Dust grain loading	SPFP	947-948	2189-2192
5.	SO_2 lab concentration	SPFP	949-950	2193-2196
6.	SO_2 control room concentration	Integer	951	2197-2198

SPFP = Single Precision Floating Point

1. Time SO_2 reading was made in an integer from 0000 hours to 2359 hours.

2. Dust Analysis flags - integer formed in the following way:

Scrubber flag *10 + inlet/outlet flag

where

Scrubber flag	Scrubber
1	TCA
2	HF
3	VENT

Inlet/Outlet flag	Meaning
1	INLET
2	OUTLET

15 March 1973
(Revised for Final Report)

Radian Project No. 200-014

MEMORANDUM

TO: F. S. LaGrone

FROM: C. T. Shelton

SUBJECT: Trip Report, Shawnee Steam Plant, 1 March 1973

Joe Barkley and Julian Jones requested that I go to Shawnee Steam Plant to make some additions to the Laboratory analysis system and to aid in determining the problems with the X-ray unit. I went to Paducah on March 1 to be there at the same time that the Siemens man was there in order to help in determining where the X-ray problems were. The Siemens man was there working on the X-ray unit when I arrived. The computer system was down when I got there.

The Disk Operating System would not boot from disk, only from mag tape, and not always from tape. The DEPOSIT NEXT switch sometimes caused the computer to start running when it was halted. The PROGRAM LOAD did not function properly with the disk. I ran several of the hardware tests to localize the problems to the above mentioned. I tried to make the ion imbalance additions requested, but the system always bombed out before I could get it done. Friday, I talked to the Data General man and explained the problems. He said he would be there Monday to work on the system. I arranged for Mike McAnally or myself to come back the week of March 5-9 when the computer was fixed in order to make the requested ion imbalance additions.

Distribution: PSL, KS, MAM, LMP, JLP, DMO

15 March 1973
(Revised for Final Report)

Radian Project No. 200-014

MEMORANDUM

TO: F. S. LaGrone

FROM: C. T. Shelton

SUBJECT: Trip Report, Shawnee Steam Plant, 9 March 1973

I returned to Paducah March 9 to make the changes requested the week before. I implemented the ion imbalance equations given on the attached sheet. The computer system had been repaired and was working properly. I was there for a short time and didn't see Joe Barkley, so I left him a

No changes in the operating procedure were required. The calculation is automatically done when a final report is requested with the FRPRT command.

Distribution: PSL, KS, MAM, LMP, JLP, DMO

PROCEDURE FOR SOLIDS IONIC IMBALANCE CALCULATION

Let the weight percentage of (1) CaO, (2) MgO, (3) CO_2, and (4) total S expressed as SO_3 be stored as W_i, i = CaO, MgO, CO_2 and SO_3. Let the molecular (formula) weights of these same species be stored in the same order in MW_i. From this, the relative sums of positive and negative charges may be calculated as Equations 1 and 2, respectively.

$$C_P = W_{CaO}/MW_{CaO} + W_{MgO}/MW_{MgO} \quad (1)$$

$$C_N = W_{CO_2}/MW_{CO_2} + W_{SO_3}/MW_{SO_3} \quad (2)$$

Any of a number of methods may be used to express the relative charge imbalance, I. An arithmetic average may be taken either with respect to the relative positive charge or with respect to the sum of the positive and negative charges, as in Equations 3 and 4.

$$I = (C_P-C_N)/C_P \quad (3)$$

$$I = 2\ (C_P-C_N)/(C_P+C_N) \quad (4)$$

10.4 APPENDIX D

TEST DATA FROM WINDSOR PILOT STUDIES

10.4.1 TEST DATA FROM LIME SLURRY SCRUBBING RUNS

10.4.1.1 CHEMICAL ANALYSES

TABLE 10.4-1 LIQUID PHASE ANALYTICAL RESULTS
CE RUN 17R

TABLE 10.4-2 SOLID PHASE ANALYTICAL RESULTS
CE TEST NO. 17R

TABLE 10.4-3 LIQUID PHASE ANALYTICAL RESULTS
CE RUN 18R

TABLE 10.4-4 SOLID PHASE ANALYTICAL RESULTS
CE EXPERIMENT 18R

TABLE 10.4-5 RESULTS OF LIQUID PHASE ANALYSES
CE EXPERIMENT 19R

TABLE 10.4-6 RESULTS OF SOLID PHASE ANALYSES
CE EXPERIMENT 19R

TABLE 10.4-7 RESULTS OF LIQUID PHASE ANALYSES
CE EXPERIMENT 20R

TABLE 10.4-8 RESULTS OF SOLID PHASE ANALYSES
CE EXPERIMENT 20R

TABLE 10.4-9 RESULTS OF LIQUID PHASE ANALYSES
CE EXPERIMENT 21R

TABLE 10.4-10 RESULTS OF SOLID PHASE ANALYSES
CE EXPERIMENT 21R

TABLE 10.4-11 RESULTS OF LIQUID PHASE ANALYSES CE EXPERIMENT 22R

TABLE 10.4-12 RESULTS OF SOLID PHASE ANALYSES CE EXPERIMENT 22R

10.4.1.2 RELATIVE SUPERSATURATIONS

TABLE 10.4-13 RELATIVE SUPERSATURATIONS CE SLURRY TESTS SERIES

TABLE 10.4-14 AMOUNT OF SEED IN SLURRY

10.4.2 TEST DATA FROM LIMESTONE SLURRY SCRUBBING RUNS

10.4.2.1 CHEMICAL ANALYSES

TABLE 10.4-15 RESULTS OF LIQUID PHASE ANALYSES EXPERIMENT 1A, 7 July 1972

TABLE 10.4-16 RESULTS OF LIQUID PHASE ANALYSES EXPERIMENT 2A, 10 July 1972

TABLE 10.4-17 RESULTS OF LIQUID PHASE ANALYSES 7 July 1972 - RUN 3A

TABLE 10.4-18 RESULTS OF LIQUID PHASE ANALYSES 11 July 1972 - RUN 1B

TABLE 10.4-19 RESULTS OF LIQUID PHASE ANALYSES 13 July 1972 - RUN 2B

TABLE 10.4-20 RESULTS OF LIQUID PHASE ANALYSES
14 July 1972 - RUN 3B

TABLE 10.4-21 RESULTS OF SOLID PHASE ANALYSES
EXPERIMENT 1A, 7 July 1972

TABLE 10.4-22 RESULTS OF SOLID PHASE ANALYSES
EXPERIMENT 2A, 10 July 1972

TABLE 10.4-23 RESULTS OF SOLID PHASE ANALYSES
7 July 1972 - RUN 3A

TABLE 10.4-24 RESULTS OF SOLID PHASE ANALYSES
11 July 1972 - RUN 1B

TABLE 10.4-25 RESULTS OF SOLID PHASE ANALYSES
13 July 1972 - RUN 2B

TABLE 10.4.26 RESULTS OF SOLID PHASE ANALYSES
14 July 1972 - RUN 3B

10.4.2.2 RELATIVE SUPERSATURATIONS

TABLE 10.4-27 RELATIVE SUPERSATURATIONS
CE SLURRY TEST SERIES

TABLE 10.4-1 - LIQUID PHASE ANALYTICAL RESULTS, CE RUN 17R

		Concentrations in Millimoles/Liter										
Sample	Date	Ca	Mg	Na	CO_3	Total S	SO_4	Cl	Total N	pH low/high	Temp. (°C)	% Ion Imbalance
Set 1 a												
Water Make Up	12/15/71	1.08	0.33	0.49				0.78	0.87			
Scrubber Liquid "T" 1	12/15/71	29.7	0.32	1.14	1.04	35.5	14.25	3.78	0.77	5.75	51.5	-3.5
Scrubber Liquid "T" 2	12/15/71	29.9		1.12		34.7	13.9			5.75	52.0	-2.4
Scrubber Liquid "T" 3	12/15/71	29.6				34.5	13.6			5.75	52.0	-2.6
Scrubber Bottom "T" 1	12/15/71	27.8	0.003	1.08	0.18	18.0	1.62	4.48		11.65	52.5	-26.8
Scrubber Bottom "T" 2	12/15/71					18.6	1.42			11.60	52.0	-22.2
Scrubber Bottom "T" 3	12/15/71					17.5	1.47			11.60	52.0	-20.5
Hold Tank Effluent	12/15/71	22.85	0.03	1.09	0.04	18.5	0.88	3.88	0.80	10.85	51.0	-1.0
Set 1												
Marble Bed Front	12/28/71	18.6	0.20	0.76	1.10	22.2	8.95	2.65	0.73	4.55/ 5.5	49.5	-0.7/-2.5
Marble Bed Back	12/28/71	22.0				25.5	8.57			5.0 / 5.4	48.5	-1.2/-2.1
Scrubber Bottoms "S"	12/28/71	16.8			0.27	12.9	1.26	2.81	0.73	10.6 /10.8	47.0	+3.0/+0.8
Spray	12/28/71	12.6	0.01	0.74	0.13	10.3	0.84	2.13		11.18	37.5	-5.3
Set 2												
Scrubber Liquid "T" 1	12/28/71	20.0	0.35	0.77	0.96	22.9	8.96	2.63		5.78/ 5.86	50.5	-1.9/-2.3
Scrubber Liquid "T" 2	12/28/71	19.7		0.75		21.7	8.13			5.75	50.0	-0.7
Scrubber Liquid "T" 3	12/28/71	19.6		0.83		22.4	9.10			5.75/ 5.85	50.0	-1.4/-1.9
Scrubber Bottom "T" 1	12/28/71	17.4	0.01	0.77	0.06	10.7	0.97	2.81		11.15/11.22	48.0	+1.4/-1.2
Scrubber Bottom "T" 2	12/28/71	17.5		0.75		10.6	1.03			11.04/11.12	48.1	+5.2/+2.9
Hold Tank Effluent	12/28/71	12.6	0.07	0.68	0.26	10.0	1.30	2.06		10.75	37.5	+1.5
Marble Bed Front	12/28/71	19.0	0.27	0.68	0.87	21.6	7.57	2.29		4.52/ 5.08	47.5	+0.4/-0.2
Marble Bed Back	12/28/71	21.95		0.75		25.2	9.23			4.45/ 4.75	46.5	+0.8/+0.5
Scrubber Bottoms "S"	12/28/71	16.0		0.74	0.20	12.6	1.30	2.39		9.9 /10.5	46.5	+5.5/+3.2
Spray	12/28/71	13.5	0.02	0.68	0.10	9.6	0.89			11.02	37.0	+3.9
Clarifier Bottom	12/28/71	16.2		0.66	0.12	8.5	0.58	0.73		11.85	25.0	+12.4
Filter Liquid	12/28/71	5.26		0.55	0.62	2.4	0.18	1.07		11.58	16.5	
Water Make Up	12/28/71	1.08		0.45								

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TABLE 10.4-2 - SOLID PHASE ANALYTICAL RESULTS, CE TEST NO. 17R

			Chemical Composition in Millimole/Gram Solid					
Sample	Date	Wt% Solids	Ca	Mg	Total S	SO_3	CO_2	% undissolved (in .04NHCl)
Set 1a								
Scrubber Liquid "T" 1	12/14/71	0.367	3.76	.493	0.907	0.49	0.323	53.4
Scrubber Liquid "T" 2	12/14/71	0.415	3.96	.491	0.938	0.49	0.316	53.0
Scrubber Liquid "T" 3	12/14/71	0.399	3.94	.504	0.923	0.45	0.399	53.2
Scrubber Bottom "T" 1	12/14/71	1.64	5.30	.443	1.12	0.82	0.430	43.9
Scrubber Bottom "T" 2	12/14/71	1.78	5.44	.419	0.907	0.65	0.398	43.6
Scrubber Bottom "T" 3	12/14/71	1.66	5.06	.432	1.02	0.71	0.407	45.6
Hold Tank Effluent	12/14/71	0.775	4.71	.412	2.445	1.92	0.513	38.7
Set 1								
Marble Bed Front	12/28/71	0.211	3.22	.522	0.869	0.80	0.220	51.3
Marble Bed Back	12/28/71	0.316						
Scrubber Bottom "S"	12/28/71	1.02	5.68	.402	0.677	0.59	0.362	35.5
Spray	12/28/71	.0078						
Set 2								
Scrubber Liquid "T" 1	12/28/71	0.274	3.40	.448	0.939	0.52	0.227	49.6
Scrubber Liquid "T" 2	12/28/71	0.251	3.68	.488	1.002	0.55	0.236	53.7
Scrubber Liquid "T" 3	12/28/71	0.269	3.57	.506	0.914	0.49	0.224	51.7
Scrubber Bottom "T" 1	12/28/71	0.850	5.52	.430	1.012	0.88	0.566	41.9
Scrubber Bottom "T" 2	12/28/71	0.904	5.59	.435	1.012	0.78	0.554	41.5
Hold Tank Effluent	12/28/71	0.327	4.57	.479	1.74	1.51	0.650	41.4
Marble Bed Front	12/28/71	0.163	3.28	.498	0.765	0.30	0.296	55.7
Marble Bed Back	12/28/71	0.293						
Scrubber Bottom "S"	12/28/71	1.11	5.80	.416	0.692	0.50	0.511	41.2
Spray	12/28/71	0.0103						
Clarifier Bottom	12/28/71	11.1	3.87	.516	2.10	1.76	0.755	40.5
Filter Liquid	12/28/71	0.0139						
Filter Solid	12/28/71	79.6	4.15	.868	0.538	0.45	0.595	40.5 *

TABLE 10.4-3 - LIQUID PHASE ANALYTICAL RESULTS, CE RUN 18R

Sample	Time	Concentrations in Millimoles/Liter Ca	Mg	Na	Total S	SO_4	Cl	pH	Temperature (°C)
Set 1									
Scrubber Liquid: T1	5.57	20.5	3.34	1.08	21.7	3.07	6.33	6.15	46.5
2	6:09	21.1	3.54	1.08	23.3	4.69		6.20	47.8
3	6:21	20.3	3.34	1.12	21.6	3.16		6.60	48.0
Scrubber Bottoms: T1	6:05	33.4		1.12	18.4	1.08	6.91	11.5	48.0
2	6:15	33.5		1.10	18.1	1.04		11.4	48.0
3	6:27	32.6		1.11	18.4	1.17		11.4	47.8
Clarifier Liquid	6:33	20.9		0.93	16.95	0.57	3.91	11.05	37.5
Hold Tank Effluent	6:38	23.3		1.06	18.3	0.80	6.17	10.75	46.0
Marble Bed: Front	6:54	22.8	3.70	1.05	23.8	2.55	6.44	6.23	43.0
Back	7:05	24.4	3.60	1.10	26.9	7.43		5.75	45.0
Scrubber Bottoms S	7:13	25.7		1.14	18.15	0.74	6.89	10.6	47.0
Scrubber Spray	7:23	23.5		1.10	18.2	0.64	6.11	10.75	46.0
Set 2									
Scrubber Liquid: T1	7:33	21.2	3.41	1.14	24.5	4.85	6.43	5.90	47.5
2	7:47	21.5	3.39	1.12	24.3	4.62		5.95	
3	7:56	22.65	3.40	1.11	25.4	5.29		5.80	48.0
Scrubber Bottoms: T1	7:39	34.3		1.13	18.5	0.97	7.15	11.45	47.5
2	7:51	35.55		1.16	18.55	0.86		11.50	
3	8:01	32.7		1.13	18.9	5.34*		11.45	
Clarifier Liquid	8:07	22.0		0.94	17.1	0.73	4.40	11.2	37.5
Hold Tank Effluent	8:11	23.9		1.11	19.0	1.31	6.28	10.6	46.0
Marble Bed: Front	8:30	26.0	3.42	1.13	30.2	7.47	6.49	6.05	45.0
Back	8:22	24.7	3.40	1.11	27.4	5.14		6.0	45.0
Scrubber Bottoms S	8:40	25.5		1.17	19.5	0.92		10.45	47.0
Scrubber Spray	8:50	23.2		1.09	19.3	0.68		10.4	47.0
Water Make-Up				0.40			0.69		

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* Probably an error.

TABLE 10.4-4 - SOLID PHASE ANALYTICAL RESULTS, CE EXPERIMENT 18R

3 February 1972

Sample		Wt.% Solids in Slurry	Composition in Millimoles/Gram					Weight % Undissolved
			Ca	Mg	SO_3	SO_4	CO_2	
Set 1								
Scrubber Liquid:	T1	4.45	4.50	0.34	2.26	0.87	0.58	34.6
	2	4.46	4.57	0.34	2.27	0.83	0.55	32.1
	3	5.28	4.60	0.34	2.18	0.86	0.50	34.8
Scrubber Bottoms:	T1	5.83	4.81	0.41	1.57	0.93	0.52	35.1
	2	6.00	4.62	0.41	1.63	0.99	0.61	35.9
	3	6.15	4.69	0.40	1.73	0.87	0.73	36.0
Clarifier Liquid		.017						
Hold Tank Effluent		4.50	4.47	0.40	2.22	0.86	0.63	34.1
Marble Bed:	Front	4.17	4.56	0.31	2.31	1.02	0.59	33.3
	Back	4.10	4.52	0.32	2.34	1.00	0.60	34.2
Scrubber Bottoms S		5.39	4.85	0.41	1.73	0.785	0.49	36.0
Scrubber Spray		3.67	4.59	0.41	2.17	0.84	0.58	34.9
Additive			5.97	0.50	0.06	0.45	0.39	46.3
Set 2								
Scrubber Liquid:	T1	4.07	4.59	0.33	2.26	1.02	0.51	34.0
	2	4.12	4.54	0.33	2.32	0.84	0.54	34.5
	3	3.93	4.49	0.33	2.36	0.84	0.58	34.6
Scrubber Bottoms:	T1	5.26	4.80	0.41	1.68	0.73	0.62	36.3
	2	5.61	4.85	0.41	1.67	0.75	0.63	36.5
	3	5.79	4.64	0.41	1.89	0.77	0.63	36.3
Hold Tank Effluent		3.66	4.57	0.41	2.12	0.865	0.64	34.0
Marble Bed:	Front	4.10	4.50	0.32	2.32	0.86	0.49	33.2
	Back	3.91	4.54	0.32	2.36	0.83	0.52	34.6
Scrubber Bottoms S		4.99	4.93	0.40	1.69	0.745	0.59	35.1
Scrubber Spray		3.35	4.47	0.40	2.20	0.88	0.54	34.6
Clarifier Bottoms			4.33	0.43	2.13	0.85	0.54	35.3

TABLE 10.4-5 - RESULTS OF LIQUID PHASE ANALYSES, CE EXPERIMENT 19R

Code No.	Sample Designation	Date & Time *	Temp. °C	pH	Total Concentrations, mmole per liter									Charge Imbalance
					Ca	Mg	Na**	Total S	Sulfite	Sulfate	Carbonate	Chloride	Nitrate ***	
SET 1														
79 80 81	Scrubber Liquid Tk 1	11:25	43.5	4.95	35.2	4.43		54.5	16.35	38.15	1.33	2.33		-9%
53	Scrubber Liquid Tk 2	11:37	43.0	5.00	35.3	4.56		53.8	28.6	25.2				-2%
85	Scrubber Liquid Tk 3	11:45	43.6	5.00	35.3	4.53		54.6	28.55	25.05				-2%
87 88 89	Scrubber Bottoms Tk 1	11:30	43.5	5.83	23.6	4.42		30.3	7.65	22.65	0.75	3.36		-3%
91	Scrubber Bottoms Tk 2	11:40	43.5	5.93	23.7	4.36		29.8	7.8	22.0				-2%
93	Scrubber Bottoms Tk 3	11:52	44.0	5.90	24.2	4.37		31.1	8.35	22.75				-3%
95 96 97	Clarifier Liquid	11:57	23.5	5.30	22.5	3.41		29.1	6.0	23.1	0.24	2.00		-3%
98 99 100	Hold Tank Effluent	12:00	39.0	5.43	24.5	4.30		36.3	15.7	20.6	1.10	2.10		-3%
102 103 104	Marble Bed: Front	12:08	41.0	4.70	34.4	4.49		53.2	27.1	26.1	1.86	2.32		-3%
106 107	Marble Bed: Back	12:15	41.5	4.50	34.4	4.52		53.4	26.6	26.8	1.83			-3%
109 110 111	Scrubber Bottoms S	12:25	44.0	5.60	27.7	4.20		37.2	14.75	24.45	0.83	3.24		-5%
113 114 115	Scrubber Spray	12:30	39.0	5.50	25.7	4.67		35.9	15.55	20.35	1.12	2.13		2%

* Samples were taken on 20 April 1972

** Spot check showed Na concentration to be ≈.40 mmoles/ℓ

*** Spot check showed NO_3 concentration to be ≈.25 mmoles/ℓ

TABLE 10.4-5 - RESULTS OF LIQUID PHASE ANALYSES, CE EXPERIMENT 19R (cont.)

					Total Concentrations, mmole per liter									
Code No.	Sample Designation	Date & Time *	Temp. C	pH	Ca	Mg	Na **	Total S	Sulfite	Sulfate	Carbonate	Chloride	Nitrate ***	Charge Imbalance
SET 2														
117 118 119	Scrubber Liquid Tk 1	12:43	44.0	5.00	35.6	4.43		55.2	26.2	29.0	1.36	2.26		-4%
121	Scrubber Liquid Tk 2	12:50	44.0	5.05	35.5	4.46		53.3	28.0	25.3				-2%
123	Scrubber Liquid Tk 3	1:05	44.0	5.00	34.9	4.35		52.9	27.75	25.15				-2%
125 126 127	Scrubber Bottoms Tk 1	12:48	44.0	6.25	21.6	4.06		25.0	4.095	20.905	0.17	3.17		
129	Scrubber Bottoms Tk 2	12:55	44.0	6.25	22.1	3.99		25.9	2.865	22.995				-1%
131	Scrubber Bottoms Tk 3	1:10	44.0	6.00	22.8	4.13		28.7	6.65	22.05				-2%
133 134 135	Clarifier Liquid	1:15	23.5	5.60	22.6	3.45		28.8	5.95	22.85	0.22	2.03		-3%
136 137 138	Hold Tank Effluent	1:20	39.0	5.50	25.5	4.23		35.9	15.05	20.85	0.97	2.03		-2%
140 141 142	Marble Bed: Front	1:30	41.5	4.9	34.5	4.40		51.9	26.35	25.55	1.83	2.30		-5%
144 145	Marble Bed: Back	1:40	42.0	4.65	34.8	4.37		52.9	25.45	27.45	1.97			-3%
147 148 149	Scrubber Bottoms S	1:45	44.0	5.6	27.6	4.24		37.3	13.65	23.65	0.83	3.25		-3%
151 152 153	Scrubber Spray	1:25	37.0	5.5	25.2	4.23		36.6	15.15	21.45	1.00	2.08		-3%

* Samples were taken on 20 April 1972

** Spot check showed Na concentration to be ≈.40 mmoles/ℓ

*** Spot check showed NO_3 concentration to be ≈.25 mmoles/ℓ

TABLE 10.4-6 - RESULTS OF SOLID PHASE ANALYSES, CE EXPERIMENT 19R

Code No.	Sample Designation	Date & Time *	Wt. % Solids in Slurry	Total S	Total Concentrations, m mole per gram					% Undissolved in 0.04 N HCl
					Calcium	Magnesium	Sulfite	Sulfate	Carbonate	
SET 1										
82	Scrubber Liquid Tk 1	11:25	1.22	1.96	3.30	0.224	1.32	0.64	0.175	53.0%
84	Scrubber Liquid Tk 2	11:37	1.22	1.90	3.31	0.222	1.29	0.61	0.166	50.2%
86	Scrubber Liquid Tk 3	11:45	1.23	1.95	3.45	0.228	1.34	0.61	0.177	50.5%
90	Scrubber Bottoms Tk 1	11:30	2.61	2.06	4.10	0.329	1.57	0.49	0.271	44.5%
92	Scrubber Bottoms Tk 2	11:40	2.73	1.64	4.93	0.321	1.28	0.36	0.240	42.3%
94	Scrubber Bottoms Tk 3	11:52	3.28	1.88	4.53	0.330	1.52	0.36	0.237	45.1
101	Hold Tank Effluent	12:00	1.39	2.26	3.83	0.200	1.60	0.66	0.172	47.7%
105	Marble Bed: Front	12:08	1.50	1.83	3.68	0.244	1.24	0.59	0.171	51.1%
108	Marble Bed: Back	12:15	1.38	1.90	3.47	0.221	1.28	0.62	0.171	51.7%
112	Scrubber Bottoms S	12:25	3.21	1.53	4.88	0.341	1.47	0.06	0.280	45.1%
116	Scrubber Spray	12:30	1.14	2.21	3.73	0.197	1.62	0.59	0.215	45.6%

* Samples were taken on 20 April 1972

TABLE 10.4-6 - RESULTS OF SOLID PHASE ANALYSES, CE EXPERIMENT 19R (cont.)

Code No.	Sample Designation	Date & Time *	Wt. % Solids in Slurry	Total S	Total Concentrations, mmole per gram					% Undissolved in 0.04 N HCl
					Calcium	Magnesium	Sulfite	Sulfate	Carbonate	
SET 2										
120	Scrubber Liquid Tk 1	12:43	1.21	1.85	3.39	0.240	1.22	0.63	0.161	51.1%
122	Scrubber Liquid Tk 2	12:50	1.35	1.84	3.52	0.243	1.23	0.61	0.209	51.9%
124	Scrubber Liquid Tk 3	1:05	1.34	1.77	3.50	0.235	1.15	0.62	0.201	50.5%
128	Scrubber Bottoms Tk 1	12:48	3.27	2.13	4.19	0.336	1.58	0.55	0.333	44.0%
130	Scrubber Bottoms Tk 2	12:55	3.54	1.85	4.72	0.334	1.37	0.48	0.349	42.0%
132	Scrubber Bottoms Tk 3	1:10	3.10	1.90	4.16	0.334	1.45	0.45	0.335	43.4%
139	Hold Tank Effluent	1:20	1.49	2.05	3.84	0.215	1.45	0.60	0.189	45.5%
143	Marble Bed: Front	1:30	1.67	1.66	3.98	0.265	1.18	0.48	0.198	48.6%
146	Marble Bed: Back	1:40	1.52	1.79	3.80	0.255	1.15	0.64	0.243	48.9%
150	Scrubber Bottoms S	1:45	4.19	1.42	5.01	0.350	1.33	0.09	0.402	42.4%
154	Scrubber Spray	1:25	1.46	2.01	4.01	0.224	1.41	0.60	0.180	45.4%
155	Fly Ash and Lime			0.45	5.81	0.500			0.455	45.8%
156	Fly Ash and Lime			0.54	5.78	0.498				47.6%

* Samples were taken on 20 April 1972

TABLE 10.4-7 - RESULTS OF LIQUID PHASE ANALYSES, CE EXPERIMENT 20R

					Total Concentrations, mmole per liter									
Code No.	Sample Designation	Date & Time *	Temp. °C	pH	Ca	Mg	Na**	Total S	Sulfite	Sulfate	Carbonate	Chloride	Nitrate***	Charge Imbalance
SET 1														
1 2 3	Scrubber Liquid Tk 1	10:36	44.5	5.20	31.6	3.37		44.9	17.85	27.05	1.36	2.13		-4%
5	Scrubber Liquid Tk 2	10:55	43.5	5.23	31.7	2.90		44.3	14.55	29.75				
7	Scrubber Liquid Tk 3	11:05	44.0	5.20	31.4	3.31	0.38	44.7	14.6	30.1				-6%
9 10 11	Scrubber Bottoms Tk 1	10:48	45.0	11.23	21.1	3.30		19.7	1.08	18.6	0.06	3.11		
13	Scrubber Bottoms Tk 2	11:00	45.0	10.82	24.3			21.3	1.03	20.3				4%
15	Scrubber Bottoms Tk 3	11:10	46.0	10.85	22.2			20.0	.93	19.1				2%
17 18 19	Clarifier Liquid	11:17	39.0	5.85	22.1	3.01		28.4	5.05	23.35	0.51	1.78		-4%
21 22 23	Hold Tank Effluent	11:25	40.0	5.75	23.6	3.24	0.38	31.9	7.45	24.45	0.95	2.03		-6%
25 26 27	Marble Bed: Front	11:40	42.5	4.7	32.0	3.44	0.40	44.9	14.75	30.15	1.49	2.23		-4%
29 30	Marble Bed: Back	11:50	42.0	4.53	32.5	3.59		46.5	15.25	31.25	1.69			-5%
32 33 34	Scrubber Bottoms S	12:00	44.0	5.93	26.1	3.32		33.4	8.1	25.3	1.38	3.01		-5%
37 38 40	Scrubber Spray	12:08	39.0	5.72	23.4	3.18		32.6	7.9	24.7	0.93	1.89		-7%

* Samples were taken on 21 April 1972

** Spot check showed Na concentration to be ≈.40 mmoles/ℓ

*** Spot check showed NO_3 concentration to be ≈.25 mmoles/ℓ

TABLE 10.4-7 - RESULTS OF LIQUID PHASE ANALYSES, CE EXPERIMENT 20R (cont.)

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Code No.	Sample Designation	Date & Time *	Temp. °C	pH	Total Concentrations, mmole per liter									Charge Imbalance
					Ca	Mg	Na**	Total S	Sulfite	Sulfate	Carbonate	Chloride	Nitrate ***	
SET 2														
43 44 45	Scrubber Liquid Tk 1	12:32	43.5	5.10	32.9	3.58		46.2	18.15	28.05	1.42	2.04		-3%
47	Scrubber Liquid Tk 2	12:45	44.0	5.05	32.6	3.54		47.8						-8%
49	Scrubber Liquid Tk 3	1:00	44.5	5.05	34.0	3.78		48.5	18.4	30.1				-4%
50 51 52	Scrubber Bottoms Tk 1	12:40	44.5	6.80	22.3	3.32		24.7	2.1	22.6	0.48	3.12		-1%
54	Scrubber Bottoms Tk 2	12:52	44.5	6.40	24.0	3.49		27.6	3.58	24.0				-2%
56	Scrubber Bottoms Tk 3	1:07	44.5	6.20	25.3	3.67		29.2						-1%
58 59 60	Clarifier. Liquid	1:20	39.0	5.80	22.9	3.28		28.7	7.4	20.9	0.57	1.95		-2%
61 62 63	Hold Tank Effluent	1:23	40.0	5.70	25.9	3.57		34.9	10.25	24.65	0.87	2.13		-4%
65 66 67	Marble Bed: Front	1:50	40.0	4.70	33.1	3.80		46.9	16.65	30.25	1.74	2.38		-4%
69 70	Marble Bed: Back	1:40	42.5	4.55	33.8	3.73		46.2	17.05	29.15	1.27			-2%
72 73 34	Scrubber Bottoms S	1:57	42.5	5.70	30.0	3.62		38.6	12.0	26.6	0.70	3.13		-3%
75 39 76	Scrubber Spray	1:30	44.5	5.87	26.6			35.7	10.2	25.5	0.98	2.03		4%

* Samples were taken on 21 April 1972

** Spot check showed Na concentration to be ~.40 mmoles/ℓ

*** Spot check showed NO_3 concentration to be ~.25 mmoles/ℓ

TABLE 10.4-8 - RESULTS OF SOLID PHASE ANALYSES, CE EXPERIMENT 20R

Code No.	Sample Designation	Date & Time *	Wt. % Solids in Slurry	Total S	Total Concentrations, mmole per gram					% Undissolved in 0.04 N HCl
					Calcium	Magnesium	Sulfite	Sulfate	Carbonate	
SET 1										
4	Scrubber Liquid Tk 1	10:36	0.735	1.67	3.18	0.300	0.98	0.69	0.205	50.3%
6	Scrubber Liquid Tk 2	10:55	0.743	1.57	3.34	0.307	0.98	0.59	0.209	51.2%
8	Scrubber Liquid Tk 3	11:05	0.691	1.58	3.79	0.370	1.03	0.55	0.172	52.2%
12	Scrubber Bottoms Tk 1	10:48	2.67	1.72	4.61	0.483	1.37	0.35	0.384	40.8%
14	Scrubber Bottoms Tk 2	11:00	1.87	1.98	4.73	0.578	1.53	0.45	0.199	42.2%
16	Scrubber Bottoms Tk 3	11:10	2.27	1.83	4.41	0.482	1.51	0.32	0.327	44.1%
20	Clarifier Liquid	11:17	0.013				0.93			
24	Hold Tank Effluent	11:25	0.738	2.05	3.73	0.241	1.44	0.61	0.201	41.9%
28	Marble Bed: Front	11:40	0.983	1.53	3.67	0.315	1.05	0.48	0.210	51.4
31	Marble Bed: Back	11:50	0.868	1.47	3.40	0.290	0.97	0.50	0.150	54.1%
36	Scrubber Bottoms S	12:00	2.53	1.36	4.87	0.364	1.20	0.16	0.249	44.3%
41	Scrubber Spray	12:08	0.694	2.00	3.77	0.251	1.42	0.58	0.181	48.8%

* Samples were taken on 21 April 1972

TABLE 10.4-8 - RESULTS OF SOLID PHASE ANALYSES, CE EXPERIMENT 20R (cont.)

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Code No.	Sample Designation	Date & Time *	Wt. % Solids in Slurry	Total S	Total Concentrations, mmole per gram					% Undissolved in 0.04 N HCl
					Calcium	Magnesium	Sulfite	Sulfate	Carbonate	
SET 2										
46	Scrubber Liquid Tk 1	12:32	0.72	1.46	2.73	0.251	0.93	0.53	0.163	55.4%
48	Scrubber Liquid Tk 2	12:45	0.703	1.42	3.08	0.290	0.95	0.47	0.204	58.3%
49A	Scrubber Liquid Tk 3	1:00	0.697	1.41	4.46	0.366	0.94	0.47	0.158	58.8%
53	Scrubber Bottoms Tk 1	12:40	2.03	1.79	3.05	0.287	1.26	0.53	0.278	45.2%
55	Scrubber Bottoms Tk 2	12:50	2.06	1.73	4.53	0.367	1.44	0.29	0.310	45.2%
57	Scrubber Bottoms Tk 3	1:07	2.06	1.59	4.28	0.362	1.24	0.35	0.346	44.0%
64	Hold Tank Effluent	1:23	0.665	1.93	3.61	0.249	1.30	0.63	0.217	47.9%
68	Marble Bed: Front	1:50	0.843	1.26	3.70	0.318	1.03	0.23	0.223	54.2
71	Marble Bed: Back	1:40	0.756	1.21	3.21	0.320	0.88	0.33	0.192	55.7%
74	Scrubber Bottoms S	1:57	2.26	1.21	4.86	3.84	1.16	0.05	0.299	49.1%
77	Scrubber Spray	1:30	0.699	1.79	3.70	0.250	1.28	0.51	0.192	49.1%

* Samples were taken on 21 April 1972

TABLE 10.4-9 - RESULTS OF LIQUID PHASE ANALYSES, CE EXPERIMENT 21R

Code No.	Sample Designation	Date & Time*	Temp. °C	pH	Total Concentrations, m mole per liter Ca	Mg	Na	Total S	Sulfite	Sulfate	Carbonate	Chloride	Nitrate	Charge Imbalance
SET 1														
157 158 159	Scrubber Liquid Tk 1	1:20	47.5	6.42	33.[illegible]	0.00		27.35	0.94	26.4	.18	9.19		1.4%
160	Scrubber Liquid Tk 2	1:32	46.0	5.92	17.5	15.6	1.11	32.40	5.05	27.4				-3.2%
161	Scrubber Liquid Tk 3	1:50	47.0	5.68	23.5	16.5		31.4	3.25	28.1				6.7%
162 163 164	Scrubber Bottoms Tk 1	1:27	45.0	9.77	26.5	0.19		23.26	0.75	22.5	.23	10.7		-3.5%
165	Scrubber Bottoms Tk 2	1:38	45.9	9.82	24.3	0.43		21.56	0.80	20.8				-4.4%
166	Scrubber Bottoms Tk 3	1:55	46.0	9.70	22.2	3.23		22.90	1.15	21.7				-5.2%
167 168 168A	Clarifier Liquid	2:00	29.0	9.85	19.4	4.30		23.16	0.85	21.3	.30	3.94		-0.6%
169 170 171	Hold Tank Effluent	2:05	45.0	8.52	18.1	11.7	1.06	27.76	1.10	26.7	.28	8.84	0.3	-3.3%
173 174 175	Marble Bed: Front	2:22	44.0	5.69	23.6	16.8		34.46	6.70	27.8	1.98	9.22		-4.1%
177 178	Marble Bed: Back	2:30	46.0	5.48	22.6	16.0		41.16	7.60	33.6	1.94			-4.6%
180 181 182	Scrubber Bottoms S	2:40	47.5	8.18	20.0	10.5		27.17	1.28	25.9	.34	10.3		-2.5%
183 184 185	Scrubber Spray	3:00	45.5	8.30	16.8	13.9		29.34	1.28	28.1	.23	8.70		-4.1%

* Samples taken on 4/26/72.

TABLE 10.4-9 - RESULTS OF LIQUID PHASE ANALYSES, CE EXPERIMENT 21R (cont.)

Code No.	Sample Designation	Date & Time*	Temp. °C	pH	Total Concentrations, mmole per liter									Charge Imbalance
					Ca	Mg	Na	Total S	Sulfite	Sulfate	Carbonate	Chloride	Nitrate	
SET 2														
188 189 190	Scrubber Liquid Tk 1	3:28	47.3	5.37	19.2	17.2		38.92	6.98	31.9	1.42	9.00		-4.5%
191	Scrubber Liquid Tk 2	3:45	47.2	5.37	19.8	16.5		46.89	10.4	36.5				-11.5%
192	Scrubber Liquid Tk 3	4:05	47.5	5.34	20.5	18.2		40.20	5.45	34.7				-3.9%
193 194 195	Scrubber Bottoms Tk 1	3:35	46.0	9.48	22.3	7.76		27.68	1.52	26.2	.19	10.3		-4.4%
196	Scrubber Bottoms Tk 2	4:00	46.0	9.47	20.2	10.5		29.26	0.8	28.5				-5.7%
197	Scrubber Bottoms Tk 3	4:10	47.0	9.35	20.8	11.1		29.60	1.3	28.3				-4.2%
198 199 200	Clarifier Liquid	4:18	29.9	9.9	17.6	4.72		21.76	0.98	20.8	.29	4.60		-3.5%
201 202 203	Hold Tank Effluent	4:23	45.0	7.03	16.9	15.1	1.09	30.50	1.73	28.8	.50	8.73	.3	-3.6%
205 206 207	Marble Bed: Front	4:33	44.0	5.5	20.5	16.8		39.71	12.9	26.8	1.89	9.13		-2.1%
209 210	Marble Bed: Back	4:42	46.5	5.38	23.6	16.6		46.35	12.0	34.4	2.04			-5.9%
212 213 214	Scrubber Bottoms S	4:52	47.8	6.42	19.4	12.0		29.05	1.12	27.9	.52	10.0		-3.3%
215 216 217	Scrubber Spray	5:00	46.0	8.90	16.9	13.9		29.11	1.32	27.8	.15	8.56		-3.6%

* Samples taken on 4/26/72.

TABLE 10.4-10 - RESULTS OF SOLID PHASE ANALYSES, CE EXPERIMENT 21R

Code No.	Sample Designation	Date & Time	Wt. % Solids in Slurry	Total S	Total Concentrations, mmole per gram					% Undissolved in 0.04 N HCl
					Calcium	Magnesium	Sulfite	Sulfate	Carbonate	
SET 1										
172	Hold Tank Effluent		8.02	3.53	4.37	.245	2.27	1.26	0.250	36.2%
176	Marble Bed: Front		8.09	3.46	4.46	.216	2.26	1.20	0.235	36.7%
179	Marble Bed: Back		9.10	3.65	4.50	.200	2.40	1.25	0.227	34.7%
186	Clarifier Bottoms			2.65	4.21	.295	1.66	0.99	0.394	32.9%
SET 2										
204	Hold Tank Effluent		6.67	3.20	4.11	.186	2.35	0.85	0.200	35.9%
208	Marble Bed: Front		7.65	3.38	4.11	.184	2.28	1.10	0.241	36.5%
211	Marble Bed: Back		7.83	3.35	4.51	.194	2.22	1.13	0.211	36.0%

TABLE 10.4-11 - RESULTS OF LIQUID PHASE ANALYSES, CE EXPERIMENT 22R

Code No.	Sample Designation	Date & Time*	Temp. °C	pH	Total Concentrations, mmole per liter									Charge Imbalance
					Ca	Mg	Na	Total S	Sulfite	Sulfate	Carbonate	Chloride	Nitrate	
SET 1														
219 220 221	Scrubber Liquid Tk 1	1:10	45.0	4.99	24.7	18.2	1.16	55.0	18.6	36.4		8.84		-7.2%
222	Scrubber Liquid Tk 2	1:25	45.0	4.94	23.6	17.9		50.93	20.4	30.53				-4.0%
223	Scrubber Liquid Tk 3	1:40	45.5	4.86	24.4	17.8		52.81	21.75	31.06				-4.3%
224 225 226	Scrubber Bottoms Tk 1	1:15	46.0	5.87	16.6	17.4		32.00	7.75	24.25		9.20		-0.4%
227	Scrubber Bottoms Tk 2	1:35	45.5	5.62	17.0	17.4		32.68	8.4	24.28				1.0%
228	Scrubber Bottoms Tk 3	1:47	46.0	5.63	18.5	18.0		37.0	8.4	28.6				-2.0%
229 230 231	Clarifier Liquid	2:00	27.0	9.11	18.9	4.18		20.7	0.77	19.93		5.09		0.2%
232 233 234	Hold Tank Effluent	2:06	46.0	5.60	16.2	18.3	1.14	31.97	7.55	24.42		8.93	.3	1.9%
236 237 238	Marble Bed: Front	2:45	45.0	6.10	18.4	17.7		37.3	4.26	29.92		9.24		-2.7%
240 241	Marble Bed: Back	2:50	45.0	5.82	20.3	18.0		41.33	6.05	35.28				-6.6%
243 244 245	Scrubber Bottoms S	2:25	44.0	8.60	17.9	17.6		33.04	1.36	31.68		8.89		-2.4%
246 247 248	Scrubber Spray	3:00	45.5	7.70	16.5	16.9		31.00	1.51	29.49		9.15		-2.6%

* Samples taken on 4/28/72.

TABLE 10.4-11 - RESULTS OF LIQUID PHASE ANALYSES, CE EXPERIMENT 22R (cont.)

Page 2

					Total Concentrations, mmole per liter									
Code No.	Sample Designation	Date & Time	Temp. °C	pH	Ca	Mg	Na	Total S	Sulfite	Sulfate	Carbonate	Chloride	Nitrate	Charge Imbalance
SET 2														
249 250 251	Scrubber Liquid Tk 1	3:06	46.0	5.27	20.9	18.4		44.34	11.5	32.84	.79	9.30		-4.8%
252	Scrubber Liquid Tk 2	3:22	46.5	5.49	20.1	18.6		39.0	8.55	30.45				-1.5%
253	Scrubber Liquid Tk 3	3:35	46.0	5.25	22.2	18.6		45.85	11.2	34.65				-4.8%
254 255 256	Scrubber Bottoms Tk 1	3:16	46.5	6.50	19.7	13.6		31.27	1.62	29.63	1.38	9.92		-3.4%
257	Scrubber Bottoms Tk 2	3:30	46.5	6.55	18.9	15.4		32.84	1.89	30.95				-4.0%
258	Scrubber Bottoms Tk 3	3:40	46.5	6.35	18.0	17.5		33.0	2.55	30.45				-2.2%
259 260 261	Clarifier Liquid	3:52	28.0	8.88	18.6	5.20		23.30	0.75	22.55	.23	5.58		-4.0%
262 623 264	Hold Tank Effluent	3:45	45.5	6.81	16.4	17.9	1.15	31.70	1.93	29.77	.65	9.56	.3	-2.3%
266 267 268	Marble Bed: Front	3:58	44.0	5.35	21.0	19.9		43.68	8.8	34.88	1.44	9.81		-4.1%
270 271 272	Scrubber Bottoms S	4:05	45.5	5.67	16.9	19.0		32.67	3.76	28.91	2.09	10.4		-0.3%
273 274	Marble Bed: Back	4:22	42.5	5.44	19.9	19.9		43.79	10.5	33.29	.90			-4.9%
276 277 278	Scrubber Spray	4:15	45.0	6.05	16.8	19.8		34.0	4.88	29.12	.62	9.75		-0.7%

* Samples taken on 4/28/72.

TABLE 10.4-12 - RESULTS OF SOLID PHASE ANALYSES, CE EXPERIMENT 22R

Code No.	Sample Designation	Date & Time	Wt. % Solids in Slurry	Total S	Total Concentrations, mmole per gram					% Undissolved in 0.04 N HCl
					Calcium	Magnesium	Sulfite	Sulfate	Carbonate	
SET 1										
235	Hold Tank Effluent		8.58	3.55	4.37	.190	2.32	1.23	0.205	35.3%
239	Marble Bed: Front		7.84	3.61	4.44	.200	2.35	1.26	0.196	35.7%
242	Marble Bed: Back		8.51	3.83	4.52	.188	2.52	1.31	0.243	35.1%
SET 2										
269	Marble Bed: Front		9.18	3.75	4.44	.172	2.40	1.35	0.146	34.9%
275	Marble Bed: Back		9.82	3.85	4.53	.155	2.51	1.34	0.133	34.6%
279	Additive			0.50	6.09	.483	0.08	0.42	0.469	47.4%

TABLE 10.4-13

RELATIVE SUPERSATURATIONS - CE SLURRY TEST SERIES

Run	Vessel		pH Range	Temp. (°C)	$a_{Ca^{++}}a_{SO_3^=}a^{.5}_{H_2O}/K_{sp}$	$a_{Ca^{++}}a_{SO_4^=}a^2_{H_2O}/K_{sp}$	$a_{Ca^{++}}a^2_{OH^-}/K_{sp}$
17R	Marble Bed:	1	4.5-5.5	49	2.1-5.2	.85-1.08	6.3×10^{-15} - 4.5×10^{-13}
		2	4.5-5.1	47	.7-2.1	.9 -1.07	2.9×10^{-15} - 5.4×10^{-14}
	Hold Tank:	1a	10.85	51	2.8	1.13	3.2×10^{-2}
		2	10.75	37.5	4.6	.5	1.9×10^{-3}
18R	Marble Bed:	1	5.75-6.2	44	4.8-7.8	1.16-1.20	8.9×10^{-13} - 5.6×10^{-12}
		2	6.0	45	7.4-11.4	1.28	$2.7\text{-}3.4\times10^{-12}$
	Hold Tank:	1	10.75	46	2.7	1.16	1×10^{-2}
		2	10.6	46	4.4	1.18	5.3×10^{-3}
19R	Marble Bed:	1	4.5-4.7	41	3.1-5.0	1.85-1.9	$2.3\text{-}5.3\times10^{-15}$
		2	4.7-4.9	42	3.5-7.4	1.8 -2.6	4×10^{-15} - 1.4×10^{-14}
	Hold Tank:	1	5.43	39	9.9	1.28	7.8×10^{-14}
		2	5.5	39	11.4	1.24	1.1×10^{-13}
20R	Marble Bed:	1	4.5-4.7	42	1.7-2.4	2.13-2.17	$2.5\text{-}5.9\times10^{-15}$
		2	4.5-4.7	41	2.1-2.9	2.03-2.13	$3.2\text{-}4.3\times10^{-15}$
	Hold Tank:	1	5.75	40	7.8	1.39	3.8×10^{-13}
		2	5.7	40	10.4	1.51	3.3×10^{-13}

TABLE 10.4-13 - RELATIVE SUPERSATURATIONS - CE SLURRY TEST SERIES (cont.)

Run	Vessel		pH Range	Temp. (°C)	$a_{Ca^{++}}a_{SO_3^=}a_{H_2O}^5/K_{sp}$	$a_{Ca^{++}}a_{SO_4}a_{H_2O}^2/K_{sp}$	$a_{Ca^{++}}a_{OH^-}^2/K_{sp}$
21R	Marble Bed:	1	5.5-5.7	45	3.9-5.6	1.39-1.61	$2.4\text{-}5.3\text{x}10^{-13}$
		2	5.4-5.5	45	5.1-6.8	1.17-1.66	$1.6\text{-}1.9\text{x}10^{-13}$
	Hold Tank:	1	8.52	45	2.95	1.25	$2.1\text{x}10^{-7}$
		2	7.03	45	3.8	1.17	$2.0\text{x}10^{-10}$
22R	Marble Bed:	1	5.8-6.1	45	5.0	1.21-1.45	$8.5\text{x}10^{-13}$ - $3\text{x}10^{-12}$
		2	5.35-5.45	45	3.4-4.7	1.26-1.43	$9.0\text{-}9.7\text{x}10^{-14}$
	Hold Tank:	1	5.6	46	4.0	.96	$3.3\text{x}10^{-13}$
		2	6.81	45	3.7	1.11	$7.0\text{x}10^{-11}$

TABLE 10.4-14
AMOUNT OF SEED IN SLURRY

(All values in weight percent)

Run	Vessel	Total Solids	$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$Ca(OH)_2$
17R	Marble Bed: 1	.26	.03	.003	.04
	2	.23	.009	.02	.04
	Hold Tank: 1a	.77	.19	.07	.10
	2	.33	.06	.01	.05
18R	Marble Bed: 1	4.13	.54	.93	.50
	2	4.00	.44	1.0	.50
	Hold Tank: 1	4.50	.50	1.05	.54
	2	3.66	.41	.80	-.49
19R	Marble Bed: 1	1.44	.23	.15	.16
	2	1.59	.25	.15	.23
	Hold Tank: 1	1.39	.29	.16	.15
	2	1.49	.28	.15	.18
20R	Marble Bed: 1	.93	.12	.08	.13
	2	.80	.10	.04	.12
	Hold Tank: 1	.74	.14	.08	.08
	2	.66	.11	.07	.07
21R	Marble Bed: 1	8.60	2.6	1.8	.45
	2	7.74	2.25	1.5	.41
	Hold Tank: 1	8.02	2.35	1.7	.35
	2	6.67	2.0	.98	.35
22R	Marble Bed: 1	8.17	2.6	1.8	.31
	2	9.50	3.0	2.2	.39
	Hold Tank: 1	8.58	2.6	1.8	.39

TABLE 10.4-15 - RESULTS OF LIQUID PHASE ANALYSES, EXPERIMENT 1A, 7 July 1972

Code #	Sample Designation	Date & Time	Temp. °C	pH	Total Concentrations, mmole per liter									% Charge Imbalance
					Ca	Mg	Na	Total S	Sulfite	Sulfate	Carbonate	Chloride	Nitrate	
SET 1														
359 360	SLT1	9:25	49.2	5.39	23.1	3.92	0.86	31.0	8.65	22.4	7.02	1.28	0.5	-2.1
362 363	SLT2	9:32	49.4	5.40	24.2	3.91	0.86	34.4	11.4	22.9	7.20	1.32	0.5	-3.6
365 366	SLT3	9:40	49.0	5.48	25.7	4.00	0.86	35.3	----	-----	8.13	1.35	0.5	----
368 369	SBT1	9:27	48.0	5.71	22.6	3.93	0.89	29.1	7.51	21.6	6.55	1.40	0.5	-2.0
371 372	SBT2	9:37	48.1	5.70	21.8	3.82	0.88	28.6	6.62	21.9	6.83	1.47	0.5	-3.2
374 375	SBT3	9:45	48.9	5.64	21.8	4.00	0.88	29.1	7.41	21.7	6.43	1.42	0.5	-2.8
377 378	CLT	9:50	32.6	6.86	17.9	2.43	0.92	19.8	1.08	18.7	4.33	1.22	0.5	-3.3
379 380	HTE	9:53	48.0	6.05	19.4	3.86	0.86	23.5	2.65	20.8	6.63	1.33	0.5	-2.6
385	MBB	10:07	47.4	5.28	27.7	4.04	0.88	42.6	22.6	20.0	3.01	1.30	---	-2.5
388 389	SB	10:15	48.2	5.27	26.9	3.92	0.89	40.4	23.8	16.6	3.49	1.34	0.5	-0.1
391 392	SS	10:20	47.7	6.10	19.1	3.80	0.88	23.0	3.04	20.0	7.77	1.29	0.5	-2.0

TABLE 10.4-15 - RESULTS OF LIQUID PHASE ANALYSES, EXPERIMENT 1A, 7 July 1972 (cont.)

Code #	Sample Designation	Date & Time	Temp. °C	pH	Total Concentrations, mmole per liter									% Charge Imbalance
					Ca	Mg	Na	Total S	Sulfite	Sulfate	Carbonate	Chloride	Nitrate	
SET 2														
394 395	SLT1	10:30	49.5	5.51	23.8	3.98	0.86	33.4	10.7	22.7	7.12	1.50	0.5	-3.7
397 398	SLT2	10:38	50.0	5.51	25.3	4.00	0.86	33.9	10.7	23.3	7.97	1.41	0.5	-2.5
400 401	SLT3	10:50	49.8	5.54	24.3	4.33	0.85	32.8	9.92	22.9	7.85	1.29	0.5	-2.6
403 404	SBT1	10:33	49.0	5.65	21.8	3.98	0.90	29.1	8.28	20.8	7.45	1.32	0.5	-2.5
406 407	SBT2	10:43	49.1	5.68	21.7	3.98	0.94	28.6	7.63	21.0	6.86	1.30	0.5	-2.4
409 410	SBT3	10:53	49.3	5.68	21.5	3.95	0.91	28.8	8.07	20.7	7.31	1.27	0.5	-2.8
412 413	CLT	10:56	33.9	6.87	17.6	2.45	0.95	19.5	1.12	18.4	5.34	1.24	0.5	-4.1
414 415	HTE	11:00	47.4	6.12	24.8	3.84	0.88	27.1	12.5	14.9	6.85	1.38	0.5	-3.2
417 417	MBF	11:15	48.5	5.31	30.2	3.97	0.91	44.3	18.9	25.4	3.98	1.22	0.5	-4.8
419 420	MBB	11:10	47.2	5.59	29.8	3.86	0.90	40.0	16.9	23.1	2.79	1.25	0.5	-1.0
422 422	SB	11:22	47.7	5.49	28.5	3.92	0.92	40.5	16.2	24.3	3.20	1.26	0.5	-3.1
424 425	SS	11:28	48.1	6.22	19.6	3.89	0.89	23.2	-----	-----	7.51	1.41	0.5	----

TABLE 10.4-16 - RESULTS OF LIQUID PHASE ANALYSES, EXPERIMENT 2A, 10 July 1972

Code	Sample Designation	Date & Time	Temp. °C	pH	Total Concentrations, mmole per liter									% Charge Imbalance
					Ca	Mg	Na	Total S	Sulfite	Sulfate	Carbonate	Chloride	Nitrate	
SET 1														
427 428	SLT1	13:45	49.0	5.29	24.5	3.55	0.87	33.4	12.4	21.0	5.79	1.39	0.5	-1.4
430 431	SLT2	14:00	49.0	5.32	24.8	3.59	0.87	33.1	12.8	20.4	7.25	1.33		-0.5
433 434	SLT3	14:12	49.0	5.30	25.2	3.56	0.87	33.7	11.7	22.1	6.25	1.31		-1.3
436 437	SBT1	13:55	48.5	5.33	23.2	3.59	0.88	30.7	9.42	21.3	5.98	1.34		-1.3
439 440	SBT2	14:07	48.5	5.32	24.0	3.58	0.88	31.2	9.83	21.4	5.65	1.39	0.5	-0.4
442 443	SBT3	14:15	49.0	5.32	25.4	4.03	0.89	37.0	----	----	5.45	1.38		----
445 446	CLT	14:25	31.0	7.19	17.5	1.84	0.98	18.7	0.74	18.0	3.39	1.14	0.5	-2.9
447 448	HTE	14:20	48.0	6.00	19.7	3.35	0.87	23.7	3.31	20.4	6.52	1.35	0.5	-2.9
450 451	MBF	14:35	48.0	4.97	30.7	3.56	0.89	44.3	21.8	22.5	3.80	1.35		-0.8
453 454	MBB	14:45	48.0	5.13	28.5	3.52	0.88	39.9	15.8	24.1	3.09	1.30	0.5	-1.8
456 457	SS	14:55	47.0	5.97	21.5	3.45	0.87	25.1	3.73	21.4	5.67	1.37		-1.9
459 460	SB	14:50	48.5	5.32	27.5	3.54	0.88	36.3	17.0	19.3	3.41	1.33		1.5

TABLE 10.4-16 - RESULTS OF LIQUID PHASE ANALYSES, EXPERIMENT 2A, 10 July 1972 (cont.) Page 2

Code #	Sample Designation	Date & Time	Temp. °C	pH	Total Concentrations, mmole per liter Ca	Mg	Na	Total S	Sulfite	Sulfate	Carbonate	Chloride	Nitrate	% Charge Imbalance
SET 2														
462 463	SLT1	15:05	49.0	5.35	24.8	3.50	0.85	33.8	13.0	20.8	6.78	1.32		-1.4
465 466	SLT2	15:15	49.0	5.33	25.3	3.53	0.87	34.2	12.3	21.9	6.76	1.30	0.5	-1.5
468 469	SLT3	15:25	49.0	5.49	25.9	3.58	0.87	35.4	12.6	22.9	5.90	1.27		-2.8
471 472	SBT1	15:10	48.5	5.34	31.4	3.56	0.88	38.5	10.5	28.1	5.40	1.25		-0.1
474 475	SBT2	15:20	48.5	5.37	24.9	3.56	0.88	33.7	10.9	22.7	5.32	1.22	0.5	-2.2
477 478	SBT3	15:35	48.5	5.52	25.8	3.58	0.88	34.0	11.7	22.3	5.07	1.20		-1.4
480 481	CLT	15:42	31.5	7.15	17.7	1.95	0.97	19.0	0.76	18.2	4.26	1.12	0.5	-3.4
482 483	HTE	15:47	47.0	6.07	20.5	3.38	0.85	24.0	3.36	20.6	5.65	1.19	0.5	-1.6
485 486	MBF	15:55	46.0	5.19	32.1	3.60	0.87	43.8	19.5	24.3	3.59	1.28		-0.4
488 489	MBB	16:02	47.0	5.24	29.4	3.52	0.88	42.4	18.6	23.8	3.93	1.18		-2.6
491 492	SS	16:10	47.0	5.29	22.5	3.56	0.87	24.6	-----	-----	6.16	1.21		----
494 495	SB	16:15	47.0	6.05	27.9	3.54	0.87	39.2	15.5	23.8	3.68	1.22	0.5	-6.4

TABLE 10.4-17 - RESULTS OF LIQUID PHASE ANALYSES, 7 July 1972, RUN 3A

Code #	Sample Designation	Date & Time	Temp. °C	pH	Total Concentrations, mmole per liter									Charge Imbalance %
					Ca	Mg	Na	Total S	Sulfite	Sulfate	Carbonate	Chloride	Nitrate	
SET 1														
301 302	SLT1	10:45	50.5	5.44	22.31	3.21	0.69	30.49	18.17	12.82	6.62	1.39	0.3	1.3
304 305	SLT2	10:55	50.5	5.51	24.07	3.22	0.68	30.78	23.9	6.88	6.65	1.42	0.3	7.0
307 308	SLT3	11:06	-	5.56	21.28	3.25	0.69	28.53	22.6	5.93	6.30	1.50	0.3	5.7
310 311	SBT1	10:50	49.5	5.62	20.13	3.18	0.66	26.58	18.3	8.28	5.73	1.51	0.3	4.3
313 314	SBT2	11:02	50.0	5.54	21.36	3.22	0.69	28.81	20.7	8.1	6.67	1.46	0.3	4.3
316 317	SBT3	11:12	-	5.62	20.26	3.21	0.69	27.14	16.7	10.44	5.85	1.35	0.3	2.4
319 320	CLT	11:15	27.5	6.99	15.83	0.90	0.90	16.82	4.02	12.8	2.01	1.36	0.3	-3.0
321 322	HTE	11:20	49.0	6.05	17.94	3.11	0.69	21.67	6.57	15.1	6.56	1.39	0.3	-1.4
324 325	MBF1	11:30	-	5.31	25.85	3.29	0.70	37.60	45.6	-	1.48	1.43	0.3	2.4
327 328	MBB1	11:42	-	5.29	24.67	3.32	0.72	34.82	21.0	13.82	2.14	1.38	0.3	2.3
330 331	SB	11:55	49.0	5.23	24.35	3.26	0.71	34.62	9.95	24.67	3.15	1.32	0.3	-5.0
333 334	SS	12:03	-	6.02	24.03	3.14	0.83	27.03	8.51	18.52	5.35	1.31	0.3	1.5

TABLE 10.4-17 - RESULTS OF LIQUID PHASE ANALYSES, 7 July 1972, RUN 3A (cont.) Page 2

Code #	Sample Designation	Date & Time	Temp. °C	pH	Total Concentrations, mmole per liter Ca	Mg	Na	Total S	Sulfite	Sulfate	Carbonate	Chloride	Nitrate	Charge Imbalance %
SET 2														
336 337	SLT1	12:25	49.5	5.46	21.61	3.16	0.71	30.50	22.2	8.3	4.44	1.34	0.3	3.9
339 340	SLT2	12:35	49.2	5.44	21.82	3.26	0.70	30.41	21.0	9.41	5.83	1.29	0.3	3.7
342 343	SLT3	12:45	-	5.44	22.58	3.30	0.71	31.97	19.7	12.27	5.18	1.30	0.3	1.6
345 346	SBT1	12:30	49.0	5.59	22.11	3.20	0.71	28.82	17.8	11.02	5.28	1.26	0.3	3.7
348 349	SBT2	12:40	-	5.51	21.57	3.21	0.70	29.73	23.0	6.73	4.48	1.31	0.3	5.2
351 352	SBT3	12:50	-	5.59	20.29	3.23	0.69	28.00	18.9	9.10	6.12	1.34	0.3	2.6
354 355	CLT	12:55	28.0	6.96	15.98	0.96	0.91	17.00	6.98	10.02	2.12	1.15	0.3	-1.9
356 357	HTE	1:00	48.5	6.02	17.80	3.18	0.69	21.67	9.62	12.05	6.36	1.32	0.3	0.6

TABLE 10.4-18 - RESULTS OF LIQUID PHASE ANALYSES, 11 July 1972, RUN 1B

					Total Concentrations, mmole per liter									
	Sample Designation	Time	Temp. °C	pH	Ca	Mg	Na	Total S	Sulfite	Sulfate	Carbonate	Chloride	Nitrate	% Charge Imbalance
SET 1	SLT1A	2:45 PM	51.3	5.68	24.66	4.54	0.70	34.80	12.68	22.12	7.50	1.19	0.5	-3.4
	SLT1B	2:50 PM	51.5	5.95	22.59	4.36	0.70	30.05	8.29	21.76	7.20	1.13	0.5	-3.8
	SLT2A	2:58 PM	51.5	5.70	24.63	4.46	0.70	34.99	12.52	22.47	5.92	1.12	0.5	-3.7
	SLT2B	3:02 PM	50.8	5.97	22.50	4.32	0.70	29.58	8.09	21.49	6.61	1.10	0.5	-3.3
	SBT1	2:55 PM	50.0	5.92	23.11	4.48	0.68	31.60	8.85	22.75	5.79	1.16	0.5	-4.3
	SBT2	3:04 PM	50.6	5.90	23.08	4.53	0.68	30.93	8.81	22.12	5.86	1.16	0.5	-3.2
	CLT	3:09 PM	37.0	7.02	19.68	3.19	0.90	21.73	2.12	19.61	4.59	1.19	0.5	-2.3
	HTE	3:12 PM	50.3	6.31	20.06	4.33	0.68	24.40	3.48	20.92	6.63	1.21	0.5	-3.2
	MBF1	3:45 PM	44.2	5.66	28.86	4.72	0.64	41.63	16.14	25.49	3.86	1.22	0.5	-4.2
	MBF2	3:25 PM	46.6	5.76	27.22	4.53	0.65	36.55	11.40	25.15	2.85	1.24	0.5	-2.7
	MBB1	3:55 PM	50.0	5.61	26.41	4.48	0.65	37.50	16.12	21.38	2.75	1.17	0.5	-2.0
	SB	3:30 PM	50.5	5.67	26.95	4.55	0.64	38.36	16.14	22.22	4.16	1.26	0.5	-2.8
	SS	3:37 PM	50.0	6.42	21.80	4.51	0.62	25.16	3.98	21.18	7.66	1.20	0.5	-2.0
SET 2	SLT1A	4:00 PM	52.0	5.82	24.19	4.73	0.68	34.31	12.35	21.96	6.39	1.23	0.5	-4.0
	SLT1B	4:06 PM	51.0	6.09	23.05	4.61	0.68	30.31	7.16	23.15	4.34	1.18	0.5	-2.8
	SLT2A	4:15 PM	51.0	6.15	22.86	4.63	0.65	30.48	7.76	22.72	4.27	1.15	0.5	-4.2
	SLT2B	4:20 PM	51.8	5.84	25.45	4.84	0.66	36.27	13.67	22.60	6.42	1.23	0.5	-4.2
	SBT1	4:10 PM	50.7	6.00	24.73	4.76	0.68	32.40	8.58	23.82	--	1.26	0.5	--
	SBT2	4:30 PM	51.0	6.00	23.14	4.74	0.64	32.33	9.51	22.82	5.58	1.29	0.5	-5.1
	CLT	4:36 PM	38.0	7.10	18.85	3.37	0.88	21.25	1.21	20.04	4.57	1.22	0.5	-3.0
	HTE	4:40 PM	50.8	5.45	19.80	4.63	0.72	24.54	3.27	21.27	6.07	1.25	0.5	0.4
	MBF1	4:47 PM	46.0	5.89	28.23	4.82	0.70	40.29	18.88	21.41	2.91	1.28	--	-3.3
	MBF2	5:12 PM	47.5	5.95	26.90	4.84	0.70	37.32	11.25	26.07	3.79	1.22	0.5	-4.8
	MBB1	4:55 PM	49.0	5.80	26.35	4.83	0.68	37.58	12.68	24.90	3.32	1.25	0.5	-4.4
	SB	5:05 PM	50.8	5.79	25.73	4.90	0.64	38.21	15.68	22.53	3.68	1.29	0.5	-4.7
	SS	5:20 PM	50.8	6.49	20.03	4.75	0.65	24.71	3.06	21.65	6.87	1.27	0.5	-4.1

TABLE 10.4-19 - RESULTS OF LIQUID PHASE ANALYSES, 13 July 1972, RUN 2B

	Sample Designation	Time	Temp. °C	pH	Total Concentrations, mmole per liter									% Charge Imbalance
					Ca	Mg	Na	Total S	Sulfite	Sulfate	Carbonate	Chloride	Nitrate	
SET 1	SLT1A	10:55 AM	51.5	5.49	23.54	5.58	0.65	34.01	11.04	22.97	--	1.36	0.5	--
	SLT1B	11:00 AM	51.4	5.79	21.84	5.45	0.68	29.96	6.01	23.95	3.76	1.34	0.5	-2.9
	SLT2A	11:09 AM	51.5	5.52	24.20	5.72	0.65	33.86	10.11	23.75	6.54	1.36	0.5	-1.7
	SLT2B	11:15 AM	51.6	5.79	22.14	5.57	0.65	30.17	6.07	24.10	3.72	1.31	0.5	-2.4
	SBT1	11:04 AM	51.3	5.49	22.84	5.76	0.65	33.46	9.20	24.26	4.77	1.35	0.5	-3.2
	SBT2	11:20 AM	51.4	5.49	23.68	5.84	0.65	33.06	9.88	23.18	4.97	1.36	0.5	-0.9
	CLT	11:25 AM	35.5	6.80	18.28	3.67	0.82	21.52	0.88	20.64	3.69	1.20	0.5	-3.0
	HTE	11:30 AM	51.2	6.04	19.40	5.67	0.66	25.44	4.03	21.41	4.91	1.36	0.5	-1.6
	MBF1	11:41 AM	46.0	5.36	26.66	5.84	0.66	39.06	15.32	23.74	3.65	1.36	0.5	-1.4
	MBF2	12:03 PM	45.5	5.81	23.97	5.84	0.68	32.43	5.81	26.62	4.34	1.34	0.5	-3.4
	MBB1	11:55 AM	48.5	5.40	25.80	5.94	0,66	37.34	9.91	27.43	4.05	1.35	0.5	-3.2
	SS	12:10 PM	50.5	6.02	19.60	5.89	0.66	25.11	3.58	21.53	5.80	1.36	0.5	-0.8
	SB	11:45 AM	50.5	5.29	26.63	5.83	0.66	37.64	15.51	22.13	3.09	1.37	0.5	0.8
SET 2	SLT1A	12:17 PM	51.0	5.50	22.90	6.04	0.67	33.21	10.48	22.73	6.01	1.36	0.5	-1.8
	SLT1B	12:21 PM	50.8	5.68	22.26	6.01	0.68	32.07	7.52	24.55	4.26	1.35	0.5	-3.3
	SLT2A	12:35 PM	50.8	5.49	23.13	6.16	0.67	33.84	10.36	23.48	6.42	1.36	0.5	-2.2
	SLT2B	12:40 PM	51.0	5.71	21.94	6.11	0.67	30.32	9.35	20.97	4.13	1.37	0.5	-0.1
	SBT1	12:30 PM	50.8	5.59	20.89	6.22	0.67	29.76	8.52	21.24	6.97	1.36	0.5	-1.1
	SBT2	12:47 PM	50.5	5.49	23.31	6.29	0.66	34.23	6.49	27.74	--	1.41	0.5	--
	CLT	12:52 PM	35.5	7.00	18.45	3.79	0.82	21.75	0.90	20.85	3.81	1.21	0.5	-3.2
	HTE	12:56 PM	50.4	6.03	18.91	6.13	0.70	25.35	3.5	21.85	5.38	1.36	0.5	-1.9
	MBF1	1:10 PM	43.0	5.59	25.85	6.25	0.70	37.35	12.87	24.48	3.75	1.33	0.5	-1.9
	MBF2	1:35 PM	46.0	5.68	23.85	6.13	0.70	32.98	6.50	26.48	3.34	1.35	0.5	-2.5
	MBB1	1:18 PM	45.8	5.45	24.57	6.07	0.68	36.75	9.96	26.79	3.28	1.36	0.5	-4.1
	SS	1:40 PM	50.0	6.10	19.22	6.23	0.66	25.30	3.34	21.96	5.40	1.37	0.5	-1.5
	SB	1:30 PM	50.7	5.31	24.13	6.28	0.70	37.43	14.29	23.14	3.59	1.37	0.5	-2.4

TABLE 10.4-20 - RESULTS OF LIQUID PHASE ANALYSES, 14 July 1972, RUN 3B

	Sample Designation	Time	Temp. °C	pH	Total Concentrations, mmole per liter									% Charge Imbalance
					Ca	Mg	Na	Total S	Sulfite	Sulfate	Carbonate	Chloride	Nitrate	
SET 1	SLT1A	9:55 AM	50.8	5.32	23.52	6.77	0.56	36.13	12.63	23.50	5.52	1.32	0.5	-2.0
	SLT1B	9:58 AM	50.6	5.58	22.58	6.50	0.58	32.64	9.05	23.59	3.84	1.33	0.5	-1.7
	SLT2A	10:06 AM	50.6	5.40	23.62	6.57	0.60	36.09	12.37	23.72	5.37	1.35	0.5	-2.4
	SLT2B	10:10 AM	50.4	5.58	22.21	6.43	0.56	33.21	8.99	24.22	3.85	1.30	0.5	-3.2
	SBT1	10:03 AM	50.0	5.31	24.27	6.72	0.60	36.98	11.74	25.24	3.58	1.37	0.5	-2.5
	SBT2	10:22 AM	50.0	5.30	26.16	6.71	0.56	39.70	Lost	--	3.31	1.31	0.5	--
	CLT	10:23 AM	36.0	6.68	18.57	4.60	0.85	22.20	1.73	20.47	4.09	1.27	0.5	-1.7
	HTE	10:31 AM	50.0	5.91	18.53	6.45	0.56	26.46	4.40	22.06	4.77	1.33	0.5	-2.7
	MBF1	10:38 AM	43.0	5.50	27.18	6.53	0.60	41.52	17.28	24.24	2.89	1.36	0.5	-2.5
	MBF2	10:52 AM	47.0	5.60	24.09	6.62	0.55	34.48	8.04	26.44	2.52	1.31	0.5	-2.4
	MBB1	10:45 AM	49.3	5.09	26.59	6.92	0.60	40.93	14.66	26.27	2.81	1.37	0.5	-2.0
	SS	11:05 AM	50.0	5.90	18.78	6.86	0.55	26.52	4.18	22.34	5.91	1.37	0.5	-2.1
	SB	10:58 AM	49.6	5.11	26.92	6.89	0.52	42.21	18.26	23.95	2.92	1.34	0.5	-1.3
SET 2	SLT1A	11:20 AM	51.0	5.29	25.49	6.79	0.49	39.14	12.82	26.32	4.01	1.35	0.5	-3.0
	SLT1B	11:25 AM	50.5	5.48	23.48	6.70	0.45	34.73	10.69	24.04	3.94	1.35	0.5	-1.9
	SLT2A	11:33 AM	50.8	5.30	24.02	6.99	0.45	37.46	15.23	22.23	5.70	1.35	0.5	-1.3
	SLT2B	11:36 AM	50.5	5.50	21.88	6.85	0.45	33.60	10.32	23.28	5.47	1.34	0.5	-2.8
	SBT1	11:30 AM	50.3	5.30	24.87	6.79	0.44	39.07	15.42	23.65	4.15	1.36	0.5	-2.3
	SBT2	11:40 AM	50.4	5.21	25.37	6.88	0.47	39.97	14.84	25.13	4.51	1.36	0.5	-2.7
	CLT	11:45 AM	37.0	6.60	18.26	4.70	0.90	22.54	2.16	20.38	4.75	1.25	0.5	-2.9
	HTE	11:50 AM	50.0	5.80	18.91	6.92	0.47	26.80	4.89	21.91	5.28	1.36	0.5	-1.4
	MBF1	12:00 PM	47.8	5.08	25.53	6.95	0.48	41.62	20.48	21.14	2.36	1.34	0.5	-0.9
	MBF2	12:10 PM	47.0	5.49	24.43	6.78	0.50	35.06	9.70	25.36	3.08	1.34	0.5	-1.3
	MBB1	12:05 PM	49.9	5.02	27.63	7.03	0.48	43.70	17.09	26.61	3.10	1.34	0.5	-2.4
	SB	12:18 PM	50.0	5.09	26.98	7.09	0.45	43.58	20.03	23.55	2.90	1.35	0.5	-6.2
	SS	12:27 PM	50.0	5.84	18.59	6.97	0.42	26.72	5.13	21.59	6.34	1.35	0.5	-2.0

TABLE 10.4-21 - RESULTS OF SOLID PHASE ANALYSES, EXPERIMENT 1A, 7 July 1972

Code #	Sample Designation	Date & Time	Wt. % Solids in Slurry	Total S	Total Concentrations, mmole per gram					% Insoluble in 0.04 HCl
					Calcium	Magnesium	Sulfite	Sulfate	Carbonate	
SET 1										
361	SLT1	9:25	6.57	3.66	8.13	0.05	2.76	0.90	4.32	2.91
364	SLT2	9:32	6.75	4.22	7.88	0.05	3.24	0.98	3.43	2.04
367	SLT3	9:40	6.79	4.19	8.11	0.05	3.16	1.03	3.70	2.18
370	SBT1	9:27	4.94	5.10	7.94	0.04	4.07	1.03	2.72	1.60
373	SBT2	9:37	5.42	4.72	7.88	0.05	3.68	1.04	3.03	1.39
376	SBT3	9:45	7.46	3.76	8.02	0.06	2.83	0.93	3.92	2.40
381	HTE	9:53	7.43	3.60	8.13	0.06	2.65	0.95	4.36	2.70
384	MBF	10:00	6.46	4.22	7.84	0.06	3.26	0.96	3.81	2.24
387	MBB	10:07	7.51	3.98	7.95	0.06	3.04	0.94	4.02	2.91
390	SB	10:15	6.92	4.07	7.93	0.06	3.17	0.90	3.79	1.64
393	SS	10:20	7.18	3.57	8.08	0.07	2.70	0.87	4.54	3.16
SET 2										
396	SLT1	10:30	6.84	3.98	7.96	0.06	3.02	0.96	3.93	2.10
399	SLT2	10:38	6.81	3.85	8.03	0.06	2.84	1.01	3.99	2.13
402	SLT3	10:50	6.77	3.90	8.00	0.06	2.96	0.94	4.09	1.85
405	SBT1	10:33	7.62	3.76	8.08	0.07	2.78	0.98	4.38	1.93
408	SBT2	10:43	7.38	3.59	8.09	0.07	2.75	0.84	4.29	2.21
411	SBT3	10:53	7.43	3.80	8.00	0.06	2.83	0.97	4.19	2.22
416	HTE	11:00	7.38	3.49	8.07	0.06	2.62	0.87	4.65	2.28
418	MBF	11:10	7.08	4.24	8.01	0.06	3.23	1.01	3.79	1.96
421	MBB	11:15	7.97	4.44	7.96	0.06	3.45	0.99	3.55	1.83
423	SB	11:22	7.49	3.69	8.12	0.06	2.76	0.93	4.50	2.72
426	SS	11:28	7.69	3.53	8.08	0.06	2.74	0.79	4.45	2.58

TABLE 10.4-22 - RESULTS OF SOLID PHASE ANALYSES, EXPERIMENT 2A, 10 July 1972

Code #	Sample Designation	Date & Time	Wt. % Solids in Slurry	Total S	Total Concentrations, mmole per gram					% Insoluble in 0.04 HCl
					Calcium	Magnesium	Sulfite	Sulfate	Carbonate	
SET 1										
429	SLT1	13:45	----	5.02	7.62	0.03	3.78	1.24	2.74	1.59
432	SLT2	14:00	----	5.01	7.82	0.04	3.74	1.27	2.91	1.55
435	SLT3	14:12	----	4.79	7.74	0.04	3.54	1.25	2.97	1.64
438	SBT1	13:55	----	5.07	7.64	0.04	3.85	1.22	2.81	1.47
441	SBT2	14:07	----	5.05	7.64	0.03	3.91	1.14	2.60	1.21
444	SBT3	14:15	----	4.64	7.80	0.04	3.52	1.12	3.17	1.60
449	HTE	14:20	----	4.59	7.83	0.04	3.39	1.20	3.23	1.80
452	MBF	14:35	----	5.02	7.72	0.04	3.76	1.26	2.75	1.53
455	MBB	14:45	----	5.26	7.67	0.03	4.02	1.24	2.57	1.43
458	SS	14:55	----	3.94	8.05	0.05	2.90	1.04	4.37	2.89
461	SB	14:50	----	4.53	7.92	0.04	3.40	1.03	3.40	2.08
SET 2										
464	SLT1	15:05	----	4.52	7.64	0.05	3.34	1.18	3.26	1.95
467	SLT2	15:15	----	4.48	7.63	0.05	3.37	1.11	3.32	1.84
470	SLT3	15:25	6.24	4.61	7.75	0.05	3.45	1.16	3.33	1.72
473	SBT1	15:10	6.67	4.71	7.81	0.05	3.53	1.18	2.82	1.51
476	SBT2	15:20	6.91	4.31	7.84	0.05	3.28	1.03	3.57	2.07
479	SBT3	15:35	5.44	4.12	7.86	0.06	3.08	1.04	3.82	2.35
484	HTE	15:47	6.43	4.12	7.71	0.06	3.14	0.98	3.61	1.93
487	MBF	15:55	7.94	4.31	7.69	0.06	3.29	1.02	3.40	1.97
490	MBB	16:02	6.65	4.45	7.60	0.05	3.38	1.07	3.38	1.95
493	SS	16:10	6.57	3.82	7.90	0.06	2.94	0.88	4.03	2.44
496	SB	16:15	----	4.43	7.68	0.06	3.37	1.06	3.40	1.73

TABLE 10.4-23 - RESULTS OF SOLID PHASE ANALYSES, 7 July 1972, RUN 3A

Code #	Sample Designation	Date & Time	Wt. % Solids in Slurry	Total S	Total Concentrations, mmole per gram					% Insoluble in 0.04 NHCl
					Calcium	Magnesium	Sulfite	Sulfate	Carbonate	
SET 1										
303	SLT1	10:45	7.18	4.60	7.18	0.034	3.50	1.10	2.73	1.97
306	SLT2	10:55	7.09	4.83	7.33	0.027	3.64	1.19	2.68	1.26
309	SLT3	11:06	7.10	4.78	7.35	0.028	3.57	1.21	2.70	1.70
312	SBT1	10:50	7.77	4.37	7.46	0.032	3.14	1.23	3.02	2.27
315	SBT2	11:02	7.63	4.44	7.33	0.031	3.33	1.11	3.24	2.01
31S	SBT3	11:12	7.83	4.46	7.36	0.031	3.33	1.13	3.00	2.27
323	HTE	11:20	7.79	4.28	7.46	0.032	3.21	1.07	3.24	2.18
326	MBF1	11:30	7.32	4.64	7.22	0.029	3.50	1.14	2.73	1.90
329	MBB1	11:42	6.32	5.39	7.32	0.023	4.02	1.37	2.08	2.05
332	SB	11:55	7.90	4.61	7.40	0.030	3.42	1.19	2.94	2.07
335	SS	12:03	7.55	4.36	7.39	0.032	3.32	1.04	3.05	2.50

TABLE 10.4-23 - RESULTS OF SOLID PHASE ANALYSES, 7 July 1972, RUN 3A (cont.) Page 2

Code #	Sample Designation	Date & Time	Wt. % Solids in Slurry	Total S	Total Concentrations, mmole per gram					% Insoluble in 0.04 NHCl
					Calcium	Magnesium	Sulfite	Sulfate	Carbonate	
SET 2										
338	SLT1	12:25	6.96	4.78	7.23	0.028	3.70	1.08	2.75	1.85
341	SLT2	12:35	7.06	4.92	7.31	0.026	3.68	1.24	2.65	1.63
344	SLT3	12:45	7.09	4.86	7.39	0.027	3.71	1.15	2.66	1.71
347	SBT1	12:30	7.59	4.96	7.30	0.026	3.74	1.22	2.46	1.70
350	SBT2	12:40	7.58	4.44	7.55	0.030	3.33	1.11	2.99	2.28
353	SBT3 - 3A	12:50	6.71	4.61	7.58	0.028	3.46	1.15	2.99	2.10
358	HTE - 3A	1:00	7.14	4.31	7.31	0.029	3.30	1.01	2.94	2.04
	Additive 1	Run 2A	100	0.002	9.50	0.11	0	0.002	9.24	2.6
	Additive 2	Run 2B	100	0.015	9.42	0.13	0	0.015	9.46	2.34
	Additive 3	Run 3B	100	0.002	9.45	0.13	0	0.002	9.40	2.26

TABLE 10.4-24 - RESULTS OF SOLID PHASE ANALYSES, 11 July 1972, RUN 1B

	Sample Designation	Time	Wt. % Solids in Slurry	Total S	Total Concentrations, mmole per gram					% Insoluble in .04 HCl
					Calcium	Magnesium	Sulfite	Sulfate	Carbonate	
SET 1	SLT1A	2:45 PM	6.00	4.19	7.84	0.06	3.16	1.03	3.63	2.32
	SLT1B	2:50 PM	5.96	4.30	7.93	0.06	3.26	1.04	3.72	2.02
	SLT2A	2:58 PM	6.07	4.28	7.79	0.06	3.22	1.06	3.66	1.90
	SLT2B	3:02 PM	6.18	4.33	7.82	0.06	3.26	1.07	3.67	1.83
	SBT1	2:55 PM	6.82	4.06	7.85	0.07	3.04	1.02	3.59	2.20
	SBT2	3:04 PM	6.38	4.12	8.03	0.07	3.10	1.02	3.82	1.66
	HTE	3:12 PM	6.17	4.02	7.88	0.07	3.04	0.98	3.74	2.12
	MBF1	3:45 PM	8.45	4.07	7.95	0.07	3.00	1.07	3.79	2.12
	MBF2	3:25 PM	6.61	4.30	7.86	0.06	3.21	1.09	3.40	1.81
	MBB1	3:55 PM	4.72	5.49	7.52	0.04	4.26	1.23	2.16	1.20
	SB	3:30 PM	6.93	4.16	7.90	0.07	3.14	1.02	3.67	2.02
	SS	3:37 PM	6.40	3.84	8.01	0.07	2.86	0.98	3.91	1.99
SET 2	SLT1A	4:00 PM	6.08	4.73	7.84	0.04	3.59	1.14	2.89	1.68
	SLT1B	4:06 PM	6.05	4.45	7.81	0.05	3.29	1.16	3.25	1.88
	SLT2A	4:15 PM	6.03	4.20	7.80	0.05	3.10	1.10	3.71	2.31
	SLT2B	4:20 PM	6.30	4.60	7.84	0.05	3.44	1.16	3.14	1.73
	SBT1	4:10 PM	6.86	4.11	7.81	0.06	3.06	1.05	3.57	2.13
	SBT2	4:30 PM	6.35	4.33	7.89	0.06	3.24	1.09	3.41	1.84
	HTE	4:40 PM	6.47	4.06	7.77	0.06	3.01	1.05	3.90	1.97
	MBF1	4:47 PM	6.61	4.18	7.76	0.06	3.11	1.07	3.53	1.96
	MBF2	5:12 PM	6.13	5.07	7.67	0.04	3.90	1.17	2.88	1.02
	MBB1	4:55 PM	4.46	5.90	7.45	0.03	4.71	1.19	1.87	0.83
	SB	5:05 PM	7.67	4.50	7.84	0.05	3.39	1.11	3.00	2.04
	SS	5:20 PM	6.71	4.21	7.92	0.06	3.13	1.08	3.48	1.64

TABLE 10.4-25 - RESULTS OF SOLID PHASE ANALYSES, 13 July 1972, RUN 2B

	Sample Designation	Time	Wt. % Solids in Slurry	Total S	Total Concentrations, mmole per gram					% Insoluble in .04 HCl
					Calcium	Magnesium	Sulfite	Sulfate	Carbonate	
SET 1	SLT1A	10:55 AM	6.82	4.70	7.75	0.05	3.40	1.30	3.04	1.67
	SLT1B	11:00 AM	7.41	4.75	7.81	0.05	3.49	1.26	2.88	1.48
	SLT2A	11:09 AM	7.60	4.80	7.70	0.05	3.45	1.35	2.96	1.54
	SLT2B	11:15 AM	7.23	4.62	7.88	0.05	3.32	1.30	3.03	1.39
	SBT1	11:04 AM	7.51	4.52	7.87	0.06	3.24	1.28	3.04	1.81
	SBT2	11:20 AM	7.68	4.61	7.74	0.06	3.33	1.28	3.04	1.70
	HTE	11:30 AM	10.05	4.51	7.62	0.08	3.25	1.26	2.93	1.76
	MBF1	11:41 AM	7.86	4.55	7.57	0.08	3.37	1.18	2.92	1.77
	MBF2	12:03 PM	11.31	5.32	7.36	0.06	3.88	1.44	2.13	1.14
	MBB	11:55 AM	6.18	6.09	7.19	0.05	4.54	1.55	1.32	0.66
	SS	12:10 PM	8.41	4.53	7.55	0.07	3.27	1.26	2.90	1.83
	SB	11:45 AM	7.09	4.80	7.54	0.06	3.45	1.35	2.73	1.49
SET 2	SLT1A	12:17 PM	7.55	5.20	7.46	0.07	3.66	1.54	2.43	1.34
	SLT1B	12:21 PM	8.63	4.68	7.63	0.07	3.32	1.36	2.77	1.66
	SLT2A	12:35 PM	6.87	4.89	7.43	0.06	3.52	1.37	2.76	1.60
	SLT2B	12:40 PM	7.75	4.83	7.52	0.07	3.41	1.42	2.73	1.65
	SBT1	12:30 PM	9.15	4.68	7.57	0.07	3.33	1.35	2.93	1.82
	SBT2	12:47 PM	11.40	4.63	7.50	0.07	3.33	1.30	2.78	1.68
	HTE	12:56 PM	8.85	4.61	7.47	0.07	3.30	1.31	2.95	1.68
	MBF1	1:10 PM	8.99	4.68	7.46	0.06	3.32	1.36	2.97	1.79
	MBF2	1:35 PM	12.34	5.60	7.30	0.04	4.10	1.50	2.00	0.98
	MBB	1:18 PM	6.87	6.05	7.22	0.03	4.50	1.55	1.34	0.76
	SS	1:40 PM	8.72	5.00	7.46	0.05	3.63	1.37	2.67	1.62
	SB	1:30 PM	9.17	5.07	7.43	0.05	3.58	1.49	2.40	1.42
	ADDITIVE 2	RUN 2B	100	0.015	9.42	0.13	0	0.015	9.46	2.34

TABLE 10.4-26 - RESULTS OF SOLID PHASE ANALYSES, 14 July 1972, RUN 3B

	Sample Designation	Time	Wt. % Solids in Slurry	Total S	Total Concentrations, mmole per gram					% Insoluble in .04 HCl
					Calcium	Magnesium	Sulfite	Sulfate	Carbonate	
SET 1	SLT1A	9:55 AM		5.83	7.08	0.04	4.13	1.70	1.40	0.96
	SLT1B	9:58 AM		5.58	7.10	0.06	3.93	1.65	1.61	1.45
	SLT2A	10:06 AM		5.75	7.13	0.05	4.02	1.73	1.50	1.25
	SLT2B	10:10 AM		5.76	7.08	0.05	4.06	1.70	1.57	1.25
	SBT1	10:03 AM		5.55	7.15	0.05	3.88	1.67	1.77	1.51
	SBT2	10:22 AM		5.50	7.09	0.05	3.86	1.64	1.88	1.58
	HTE	10:31 AM		5.63	7.16	0.05	3.94	1.69	1.82	1.46
	MBF1	10:38 AM		5.81	7.01	0.05	4.04	1.77	1.49	1.21
	MBF2	10:52 AM		6.10	7.10	0.04	4.30	1.80	1.19	1.00
	MBB	10:45 AM		6.46	7.04	0.03	4.62	1.84	0.87	0.64
	SS	11:05 AM		5.70	7.15	0.05	3.87	1.83	1.67	1.40
	SB	10:58 AM		5.66	7.17	0.05	3.89	1.77	1.82	1.34
SET 2	SLT1A	11:20 AM		5.76	7.12	0.05	4.01	1.75	1.50	1.40
	SLT1B	11:25 AM		5.76	7.13	0.04	4.07	1.69	1.66	1.36
	SLT2A	11:33 AM		5.86	7.06	0.04	4.03	1.83	1.43	1.28
	SLT2B	11:36 AM		5.89	7.17	0.05	3.98	1.91	1.38	1.35
	SBT1	11:30 AM		5.57	7.17	0.05	3.83	1.74	1.70	1.72
	SBT2	11:40 AM		5.71	7.13	0.05	3.95	1.76	1.49	1.45
	HTE	11:50 AM		5.67	7.14	0.05	3.94	1.73	1.64	1.51
	MBF1	12:00 PM		5.88	7.10	0.05	4.06	1.82	1.27	1.26
	MBF2	12:10 PM		6.12	7.03	0.05	4.25	1.87	1.33	0.99
	MBB	12:05 PM		6.39	7.00	0.04	4.56	1.83	0.86	0.71
	SB	12:18 PM		5.95	7.09	0.04	4.17	1.76	1.27	1.22
	SS	12:27 PM		5.63	7.13	0.06	3.91	1.72	1.68	1.85
	ADDITIVE 3	RUN 3B	100	0.002	9.45	0.13	0	0.002	9.40	2.26

TABLE 10.4-27

RELATIVE SUPERSATURATIONS - CE SLURRY TEST SERIES

Run	Vessel	Set	pH	Temp (°C)	$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaCO_3$
1A	Marble Bed	1	5.28	47.4	10.6	1.22	0.012
		2	5.59	47.2	14.0	1.41	0.039
	Hold Tank	1	6.05	48.0	3.5	1.09	0.41
		2	6.12	47.4	2.0	0.87	0.62
2A	Marble Bed	1	4.97	48.0	5.9	1.45	0.043
		2	5.19	46.0	8.6	1.57	0.010
	Hold Tank	1	6.00	48.0	4.1	1.09	0.34
		2	6.07	47.0	4.8	1.12	0.37
3A	Marble Bed	1	5.29	49.0	9.6	0.87	0.010
	Hold Tank	1	6.05	49.0	8.4	0.80	0.40
		2	6.02	48.5	11.9	0.64	0.35
1B	Upper Marble Bed	1	5.76	46.6	11.6	1.43	0.068
		2	5.95	47.5	14.2	1.45	0.181
	Lower Marble Bed	1	5.64	47.1	13.6	1.40	0.050
		2	5.90	47.5	17.9	1.28	0.103
	Hold Tank	1	6.31	50.3	5.9	1.07	1.080
		2	5.45	50.8	1.6	1.12	0.042
2B	Upper Marble Bed	1	5.81	45.5	6.0	1.40	0.011
		2	5.68	46.0	5.5	1.39	0.052
	Lower Marble Bed	1	5.38	47.3	6.6	1.42	0.021
		2	5.52	44.4	7.9	1.38	0.029
	Hold Tank	1	6.04	51.2	4.9	1.05	0.33
		2	6.03	50.4	4.2	1.05	0.33
3B	Upper Marble Bed	1	5.60	47.0	5.8	1.38	0.030
		2	5.49	47.0	5.9	1.35	0.024
	Lower Marble Bed	1	5.30	46.2	8.2	1.40	0.013
		2	5.05	48.9	5.2	1.33	0.004
	Hold Tank	1	5.91	50.0	4.3	1.03	0.178
		2	5.80	50.0	4.2	1.03	0.133

10.5 APPENDIX E

SAMPLE CALCULATIONS ON WINDSOR TEST DATA

10.5.1 SAMPLE CALCULATIONS FOR LIME SLURRY SCRUBBING TESTS

TABLE 10.5-1 TOTAL SULFUR MATERIAL BALANCES
EXPERIMENT 17R

TABLE 10.5-2 RATE CALCULATIONS USING SOLID BALANCE
EXPERIMENT 17R

10.5.2 SAMPLE CALCULATIONS FOR LIMESTONE SLURRY SCRUBBING TESTS

TABLE 10.5-3 TOTAL SULFUR MATERIAL BALANCE
EXPERIMENTS 1A and 2A

TABLE 10.5-4 RATE CALCULATIONS USING LIQUID
SPECIES BALANCES - EXPERIMENT 1A

TABLE 10.5-1 - TOTAL SULFUR MATERIAL BALANCES, EXPERIMENT 17R

Scrubber	Stream Name	Flow Rate	Total S in Gas (ppm)	Solids Content	Total S in Solids (mmole/g)	Total S in Liquid (mmole/ℓ)	Total S (gmole/min)
Set 1							
Incoming Streams	Inlet Gas	11,000 gmole/min	1500	----	----	----	16.5
	Scrubber Spray	416 ℓ/min	----	----	----	10.3	4.3
	Additive	2,010 g/min	----	100%	.51	----	1.0
Outgoing Streams	Outlet Gas	11,600 gmole/min	750	----	----	----	8.7
	Downcomer	329 ℓ/min	----	2.11 g/ℓ	.87	22.2	8.6(avg.)
	(Marble Bed Samples)			3.16 g/ℓ		25.5	
	Bottoms	102 ℓ/min	----	10.3 g/ℓ	.68	12.9	2.0
			Σ Total S In = 21.8	Σ Total S Out = 19.3			
Set 2							
Incoming Streams	Inlet Gas	11,000 gmole/min	1500	----	----	----	16.5
	Scrubber Spray	416 ℓ/min	----	----	----	9.6	4.0
	Additive	2,010 g/min	----	100%	.51	----	1.0
Outgoing Streams	Outlet Gas	11,600 gmole/min	750	----	----	----	8.7
	Downcomer	329 ℓ/min	----	1.63 g/ℓ	.765	21.6	8.3(avg.)
				2.93 g/ℓ		25.2	
	Bottoms	102 ℓ/min	----	11.7 g/ℓ	.69	12.6	2.1
			Σ Total S In = 21.5	Σ Total S Out = 19.1			

TABLE 10.5-1 - TOTAL SULFUR MATERIAL BALANCES, EXPERIMENT 17R (cont.)

Hold Tank	Stream Name	Flow Rate (ℓ/min)	Solids Content (g/ℓ)	Total S in Solids (mmole/g)	Total S in Liquid (mmole/ℓ)	Total S (gmole/min)
Set 1a*						
Incoming Streams	Scrubber Liquid	529	3.68	.91	35.5	20.4(avg.)
	(Downcomer)		4.16	.94	34.7	
			4.00	.92	34.5	
	Scrubber Bottoms	113.5	16.5	1.12		4.0(avg.)
			18.0	.91		
			16.7	1.02		
Outgoing Stream	Hold Tank Effluent	643	7.78	2.45	18.5	24.1
		Σ Total S In = 24.4		Σ Total S Out = 24.1		
Set 2						
Incoming Streams	Scrubber Liquid	329	2.74	.94	22.9	8.2(avg.)
			2.51	1.00	21.7	
			2.69	.91	22.4	
	Scrubber Bottoms	102	8.50	1.01	10.7	2.0(avg.)
			9.08	1.01	10.6	
	Make-Up Water	117 (By Difference)	----	----	----	----
Outgoing Stream	Hold Tank Effluent	548	3.27	1.74	10.0	8.6
		Σ Total S In = 10.2		Σ Total S Out = 8.6		

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* Set 1a Hold tank samples were taken independently of all other samples for Run 17R.

TABLE 10.5-2 - RATE CALCULATIONS USING SOLID BALANCE, EXPERIMENT 17R

	Vessel	Reaction	Method of Calculation	Stream Name		Stream Flow Rate	Solid Content	Total Species in Solid (mmoles/g)	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
17R, Set 1	Marble Bed	$CaSO_3 \cdot \frac{1}{2}H_2O$ Precipitation	Solid SO_3 Balance	Incoming Streams	No Sulfite Solids in Incoming Streams						
				Outgoing Streams	Downcomer*	329 ℓ/min	2.11 g/ℓ 3.16 g/ℓ	0.80 SO_3			693 SO_3
					Bottoms	102 ℓ/min	10.3 g/ℓ	0.59 SO_3			620 SO_3
				$CaSO_3 \cdot \frac{1}{2}H_2O$ Precipitation Rate	= Σ SO_3(solid)Out - Σ SO_3(solid)In = 693 + 620 = 1310 mmole/min						
		SO_2 Oxidation	Gas/Liquid SO_2 Balance - Precipitation Rate	Incoming Streams	Inlet Flue Gas	11,000 gmoles/min				1500 SO_2	16,500 SO_2
					Scrubber Spray	406 ℓ/min			0.84 SO_2		340 SO_2
				Outgoing Streams	Outlet Flue Gas	11,600 gmoles/min				750 SO_2	8,700 SO_2
					Downcomer	329 ℓ/min			8.95 SO_2 8.57 SO_2		2,880 SO_2
					Bottoms	102 ℓ/min			1.26 SO_2		130 SO_2
		SO_2 Oxidation Rate	= Σ SO_2(gas + liquid)In - Σ SO_2(gas + liquid)Out - Precipitation Rate of $CaSO_3 \cdot \frac{1}{2}H_2O$ = 16,840 - 11,710 - 1,310 = 3820 mmole/min									
		$CaSO_4 \cdot 2H_2O$ Precipitation	Solid SO_4 Balance	Incoming Streams	Additive	2,010 g/min		0.5 SO_4			1,005 SO_4
				Outgoing Streams	Downcomer	329 ℓ/min	2.11 g/ℓ 3.16 g/ℓ	0.07 SO_4			61 SO_4
					Bottoms	102 ℓ/min	10.3 g/ℓ	0.09 SO_4			95 SO_4
				$CaSO_4 \cdot 2H_2O$ Precipitation Rate	= Σ SO_4(solid)Out - Σ SO_4(solid)In = 156 mmole/min - 1005 mmole/min = -850 mmole/min						
		$CaCO_3$ Precipitation	Solid CO_3 Balance	Incoming Streams	Additive	245 g/min		0.39 CO_3			95 CO_3

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* All Downcomer values are an average of two marble bed samples.

TABLE 10.5-2 - RATE CALCULATIONS USING SOLID BALANCE, EXPERIMENT 17R (cont.)

	Vessel	Reaction	Method of Calculation		Stream Name	Stream Flow Rate	Solid Content	Total Species in Solid (mmoles/g)	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
17R, Set 1 (cont.)	Marble Bed	$CaCO_3$ Precipitation	Solid CO_2 Balance	Outgoing Streams	Downcomer	329 ℓ/min	2.11 g/ℓ 3.16 g/ℓ	0.22 CO_2			191 CO_2
					Bottoms	102 ℓ/min	10.3 g/ℓ	0.36 CO_2			378 CO_2

$CaCO_3$ Precipitation Rate $= \Sigma\ CO_2(\text{solid})\text{Out} - \Sigma\ CO_2(\text{solid})\text{In}$
$= 569 - 95 = 474$ mmole/min

		$Ca(OH)_2$ Dissolution	Liquid Ca Balance + Σ Precipitation	Incoming Streams	Scrubber Spray	406 ℓ/min			12.6 Ca		5,110 Ca
				Outgoing Streams	Downcomer	329 ℓ/min			18.6 Ca 22.0 Ca		6,680 Ca
					Bottoms	102 ℓ/min			16.8 Ca		1,710 Ca

$Ca(OH)_2$ Dissolution Rate $= \Sigma\ Ca(\text{liquid})\text{Out} - \Sigma\ Ca(\text{liquid})\text{In} + \Sigma$ Ca Precipitation Reactions
$= 9390 - 5110 + 930 = 5210$ mmole $Ca(OH)_2$/min

	*Hold Tank	$CaSO_3 \cdot \frac{1}{2}H_2O$ Precipitation	Solid SO_2 Balance	Incoming Streams	Scrubber Liquid	529 ℓ/min	3.68 g/ℓ 4.16 g/ℓ 4.00 g/ℓ	0.49 SO_2 0.49 SO_2 0.45 SO_2			996 SO_2
					Scrubber Bottoms	114 ℓ/min	16.5 g/ℓ 18.0 g/ℓ 16.7 g/ℓ	0.82 SO_2 0.65 SO_2 0.71 SO_2			1,415 SO_2
				Outgoing Streams	Hold Tank Effluent	643 ℓ/min	7.78 g/ℓ	1.92 SO_2			9,590 SO_2

$CaSO_3 \cdot \frac{1}{2}H_2O$ Precipitation Rate $= \Sigma\ SO_2(\text{solid})\text{Out} - \Sigma\ SO_2(\text{solid})\text{In}$
$= 9590 - 2410 = 7180$ mmole $CaSO_3 \cdot \frac{1}{2}H_2O$/min

		SO_2 Oxidation	Liquid SO_2 Balance - Precipitation	Incoming Streams	Scrubber Liquid	529 ℓ/min			14.25 SO_2 13.9 SO_2 13.6 SO_2		7,370 SO_2
					Scrubber Bottoms	114 ℓ/min			1.62 SO_2 1.42 SO_2 1.47 SO_2		170 SO_2
				Outgoing Streams	Hold Tank Effluent	643 ℓ/min			0.88 SO_2		565 SO_2

SO_2 Oxidation Rate $= \Sigma\ SO_2(\text{liquid})\text{In} - \Sigma\ SO_2(\text{liquid})\text{Out} - CaSO_3 \cdot \frac{1}{2}H_2O$ Precipitation Rate
$= 7540 - 565 - 7180 = -205$ mmole/min

* The hold tank samples for Set 1 were taken independently of the remaining sample sets before the use of blowdown was initiated.

TABLE 10.5-2 - RATE CALCULATIONS USING SOLID BALANCE, EXPERIMENT 17R (cont.)

	Vessel	Reaction	Method of Calculation		Stream Name	Stream Flow Rate	Solid Content	Total Species in Solid (mmoles/g)	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
17R, Set 1 (cont.)	Hold Tank	$CaSO_4 \cdot 2H_2O$ Precipitation	Solid SO_4 Balance	Incoming Streams	Scrubber Liquid	529 ℓ/min	3.68 g/ℓ 4.16 g/ℓ 4.00 g/ℓ	0.42 SO_4 0.45 SO_4 0.47 SO_4			933 SO_4
					Scrubber Bottoms	114 ℓ/min	16.5 g/ℓ 18.0 g/ℓ 16.7 g/ℓ	0.30 SO_4 0.26 SO_4 0.31 SO_4			564 SO_4
				Outgoing Streams	Hold Tank Effluent	643 ℓ/min	7.78 g/ℓ	0.525 SO_4			2,625 SO_4

$CaSO_4 \cdot 2H_2O$ Precipitation Rate $= \Sigma\ SO_4(\text{solid})\text{Out} - \Sigma\ SO_4(\text{solid})\text{In}$

$= 2625 - 1500 = 1125$ mmole $CaSO_4 \cdot 2H_2O$/min

	Vessel	Reaction	Method of Calculation		Stream Name	Stream Flow Rate	Solid Content	Total Species in Solid (mmoles/g)	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
		$CaCO_3$ Precipitation	Solid CO_2 Balance	Incoming Streams	Scrubber Liquid	529 ℓ/min	3.68 g/ℓ 4.16 g/ℓ 4.00 g/ℓ	0.32 CO_2 0.32 CO_2 0.40 CO_2			723 CO_2
					Scrubber Bottoms	114 ℓ/min	16.5 g/ℓ 18.0 g/ℓ 16.7 g/ℓ	0.43 CO_2 0.40 CO_2 0.41 CO_2			803 CO_2
				Outgoing Streams	Hold Tank Effluent	643 ℓ/min	7.78 g/ℓ	0.51 CO_2			2,550 CO_2

$CaCO_3$ Precipitation Rate $= \Sigma\ CO_2(\text{solid})\text{Out} - \Sigma\ CO_2(\text{solid})\text{In}$

$= 2550 - 1526 = 1024$ mmole $CaCO_3$/min

	Vessel	Reaction	Method of Calculation		Stream Name	Stream Flow Rate	Solid Content	Total Species in Solid (mmoles/g)	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
		$Ca(OH)_2$ Dissolution	Liquid Ca Balance + Σ Precipitation	Incoming Streams	Scrubber Liquid	529 ℓ/min			29.7 Ca 29.9 Ca 29.6 Ca		15,700 Ca
					Scrubber Bottoms	114 ℓ/min			27.8 Ca		3,170 Ca
				Outgoing Streams	Hold Tank Effluent	643 ℓ/min			22.8 Ca		14,690 Ca

$Ca(OH)_2$ Dissolution $= \Sigma\ Ca(\text{liquid})\text{Out} - \Sigma\ Ca(\text{liquid})\text{In} + \Sigma$ Precipitation Rates

$= 14690 - 18870 + 9330 = 5050$ mmole $Ca(OH)_2$/min

TABLE 10.5-2 - RATE CALCULATIONS USING SOLID BALANCE, EXPERIMENT 17R (cont.)

	Vessel	Reaction	Method of Calculation		Stream Name	Stream Flow Rate	Solid Content	Total Species in Solid (mmoles/g)	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
17R, Set 2	Marble Bed	$CaSO_3 \cdot \frac{1}{2}H_2O$	Solid SO_2 Balance	Incoming Streams	No Sulfite solids in entering streams.						
				Outgoing Streams	Downcomer	329 ℓ/min	1.63 g/ℓ 2.93 g/ℓ	0.30 SO_2			225 SO_2
					Bottoms	106 ℓ/min	11.7 g/ℓ	0.50 SO_2			620 SO_2

$CaSO_3 \cdot \frac{1}{2}H_2O$ Precipitation Rate = $\Sigma\ SO_2$(solid)Out - $\Sigma\ SO_2$(solid)In
= 845 mmole $CaSO_3 \cdot \frac{1}{2}H_2O$/min

	Vessel	Reaction	Method of Calculation		Stream Name	Stream Flow Rate	Solid Content	Total Species in Solid (mmoles/g)	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
		SO_2 Oxidation	Gas/Liquid Balance - $CaSO_3$ Precipitation	Incoming Streams	Inlet Flue Gas	11,000 gmole/min				1500 SO_2	16,500 SO_2
					Scrubber Spray	406 ℓ/min			0.89 SO_2		361 SO_2
				Outgoing Streams	Outlet Flue Gas	11,600 gmole/min				770 SO_2	8,930 SO_2
					Downcomer	329 ℓ/min			7.57 SO_2 9.23 SO_2		2,765 SO_2
					Bottoms	106 ℓ/min			1.30 SO_2		138 SO_2

SO_2 Oxidation Rate = $\Sigma\ SO_2$(liquid)In - $\Sigma\ SO_2$(liquid)Out - Precipitation Rate of $CaSO_3 \cdot \frac{1}{2}H_2O$
= 16860 - 11830 - 845 = 4185 mmole SO_2/min

	Vessel	Reaction	Method of Calculation		Stream Name	Stream Flow Rate	Solid Content	Total Species in Solid (mmoles/g)	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
		$CaSO_4 \cdot 2H_2O$ Precipitation	Solid SO_4 Balance	Incoming Streams	Additive	2,010 g/min		0.5 SO_4			1,005 SO_4
				Outgoing Streams	Downcomer	329 ℓ/min	1.63 g/ℓ 2.93 g/ℓ	0.465 SO_4			349 SO_4
					Bottoms	102 ℓ/min	11.7 g/ℓ	0.192 SO_4			229 SO_4

$CaSO_4 \cdot 2H_2O$ Precipitation Rate = $\Sigma\ SO_4$(solid)Out - $\Sigma\ SO_4$(solid)In
= 578 - 1005 ≅ -430 mmole/min

	Vessel	Reaction	Method of Calculation		Stream Name	Stream Flow Rate	Solid Content	Total Species in Solid (mmoles/g)	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
		$CaCO_3$ Precipitation	Solid CO_3 Balance	Incoming Streams	Additive	2,010 g/min		0.39 CO_3			783 CO_3
				Outgoing Streams	Downcomer	329 ℓ/min	1.63 g/ℓ 2.93 g/ℓ	0.296 CO_3			222 CO_3
					Bottoms	102 ℓ/min	11.7 g/ℓ	0.511 CO_3			608 CO_3

$CaCO_3$ Precipitation Rate = $\Sigma\ CO_3$(solid)Out - $\Sigma\ CO_3$(solid)In
= 830 - 783 = Essentially Zero

TABLE 10.5-2 - RATE CALCULATIONS USING SOLID BALANCE, EXPERIMENT 17R (cont.)

	Vessel	Reaction	Method of Calculation	Streams	Stream Name	Stream Flow Rate	Solid Content	Total Species in Solid (mmoles/g)	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
17R, Set 2 (cont.)	Marble Bed	$Ca(OH)_2$ Dissolution	Liquid Ca Balance + Σ Precipitation	Incoming Streams	Scrubber Spray	406 ℓ/min			13.5 Ca		5,480 Ca
				Outgoing Streams	Downcomer	329 ℓ/min			19.0 Ca 21.95 Ca		6,730 Ca
					Bottoms	102 ℓ/min			16.0 Ca		1,632 Ca

$Ca(OH)_2$ Dissolution = Σ Ca(liquid)Out - Σ Ca(liquid)In + Σ Ca Precipitation Rates
= 8362 - 5480 + 415 ≅ 3300 mmole/min

	Vessel	Reaction	Method of Calculation	Streams	Stream Name	Stream Flow Rate	Solid Content	Total Species in Solid (mmoles/g)	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
	Hold Tank	$CaSO_3 \cdot \frac{1}{2}H_2O$ Precipitation	SO_3 Solids Balance	Incoming Streams	Scrubber Liquid	329 ℓ/min	2.74 g/ℓ 2.51 g/ℓ 2.69 g/ℓ	0.52 SO_3 0.55 SO_3 0.49 SO_3			Avg. 453 SO_3
					Scrubber Bottoms	102 ℓ/min	8.50 g/ℓ 9.08 g/ℓ	0.88 SO_3 0.78 SO_3			Avg. 744 SO_3
				Outgoing Streams	Hold Tank Effluent	548 ℓ/min	3.27 g/ℓ	1.51 SO_3			2,710 SO_3

$CaSO_3 \cdot \frac{1}{2}H_2O$ Precipitation Rate = Σ SO_3(solid)Out - Σ SO_3(solid)In
= 2710 - 1200 = 1510 mmole $CaSO_3 \cdot \frac{1}{2}H_2O$/min

	Vessel	Reaction	Method of Calculation	Streams	Stream Name	Stream Flow Rate	Solid Content	Total Species in Solid (mmoles/g)	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
		SO_2 Oxidation	Liquid SO_2 Balance - Precipitation Rate	Incoming Streams	Scrubber Liquid	329 ℓ/min			8.96 SO_2 8.13 SO_2 9.10 SO_2		Avg. 2,870 SO_2
					Scrubber Bottoms	102 ℓ/min			0.97 SO_2 1.03 SO_2		Avg. 102 SO_2
				Outgoing Streams	Hold Tank Effluent	548 ℓ/min			1.30 SO_2		713 SO_2

SO_2 Oxidation Rate = Σ SO_2(liquid)In - Σ SO_2(liquid)Out - $CaSO_3 \cdot \frac{1}{2}H_2O$ Precipitation Rate
= 2970 - 710 - 1510 = 750 mmole SO_2/min

	Vessel	Reaction	Method of Calculation	Streams	Stream Name	Stream Flow Rate	Solid Content	Total Species in Solid (mmoles/g)	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
		$CaSO_4 \cdot 2H_2O$ Precipitation Rate	Solid SO_4 Balance	Incoming Streams	Scrubber Liquid	329 ℓ/min	2.74 g/ℓ 2.51 g/ℓ 2.69 g/ℓ	0.42 SO_4 0.45 SO_4 0.42 SO_4			Avg. 375 SO_4
					Scrubber Bottoms	102 ℓ/min	8.50 g/ℓ 9.08 g/ℓ	0.13 SO_4 0.23 SO_4			Avg. 162 SO_4
				Outgoing Streams	Hold Tank Effluent	548 ℓ/min	3.27 g/ℓ	0.23 SO_4			412 SO_4

$CaSO_4 \cdot 2H_2O$ Precipitation Rate = Σ SO_4(solid)Out - Σ SO_4(solid)In
= 412 - 537 = -125 mmole $CaSO_4 \cdot 2H_2O$/min

TABLE 10.5-2 - RATE CALCULATIONS USING SOLID BALANCE, EXPERIMENT 17R (cont.)

	Vessel	Reaction	Method of Calculation		Stream Name	Stream Flow Rate	Solid Content	Total Species in Solid (mmoles/g)	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
17R, Set 2 (cont.)	Hold Tank	CaCO$_3$ Precipitation Rate	Solid CO$_2$ Balance	Incoming Streams	Scrubber Liquid	329 ℓ/min	2.74 g/ℓ 2.51 g/ℓ 2.69 g/ℓ	0.23 CO$_2$ 0.24 CO$_2$ 0.22 CO$_2$			Avg. 200 CO$_2$
					Scrubber Bottoms	102 ℓ/min	8.50 g/ℓ 9.08 g/ℓ	0.57 CO$_2$ 0.55 CO$_2$			Avg. 502 CO$_2$
				Outgoing Streams	Hold Tank Effluent	548 ℓ/min	3.27 g/ℓ	0.65 CO$_2$			1,165 CO$_2$

CaCO$_3$ Precipitation Rate = Σ CO$_2$(solid)Out - Σ CO$_2$(solid)In
= 1165 - 700 = 465 mmole CaCO$_3$/min

	Vessel	Reaction	Method of Calculation		Stream Name	Stream Flow Rate	Solid Content	Total Species in Solid (mmoles/g)	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
		Ca(OH)$_2$ Dissolution	Liquid Ca Balance + Σ Precipitation Rate	Incoming Streams	Scrubber Liquid	329 ℓ/min			20.0 Ca 19.7 Ca 19.6 Ca		Avg. 6,500 Ca
					Scrubber Bottoms	102 ℓ/min			17.4 Ca 17.5 Ca		Avg. 1,780 Ca
					Make-Up Water	117 ℓ/min			1.08 Ca		126.5 Ca
				Outgoing Streams	Hold Tank Effluent	548 ℓ/min			12.6 Ca		6,900 Ca

Ca(OH)$_2$ Dissolution Rate = Σ Ca(liquid)Out - Σ Ca(liquid)In + Σ Ca Precipitation Rate
= 6900 - 8410 + 1850 = 340 mmole Ca(OH)$_2$/min

	Vessel	Reaction	Method of Calculation		Stream Name	Stream Flow Rate	Solid Content	Total Species in Solid (mmoles/g)	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
		Ca(OH)$_2$ Dissolution	Solid Ca Balance + Σ Precipitation Rate	Incoming Streams	Scrubber Liquid	329 ℓ/min	2.74 g/ℓ 2.51 g/ℓ 2.69 g/ℓ	3.40 Ca 3.68 Ca 3.57 Ca			Avg. 3,095 Ca
					Scrubber Bottoms	102 ℓ/min	8.50 g/ℓ 9.08 g/ℓ	5.52 Ca 5.59 Ca			Avg. 4,980 Ca
				Outgoing Streams	Hold Tank Effluent	548 ℓ/min	3.27 g/ℓ	4.57 Ca			8,190 Ca

Ca(OH)$_2$ Dissolution Rate = Σ Ca(solid)In - Σ Ca(solid)Out + Σ Ca Precipitation Rates
= 8075 - 8190 + 1850 = 1965 mmole Ca(OH)$_2$/min

TABLE 10.5-3 - TOTAL SULFUR MATERIAL BALANCE, EXPERIMENTS 1A AND 2A

	Vessel	Stream Name		Stream Flow Rate	Total S in Gas (ppm)	Solids Content (g/ℓ)	Total S in Solids (mmoles/g)	Total S in Liquid (mmoles/ℓ)	Total S (gmoles/min)
RUN 1									
Set 1	Scrubber	Incoming Streams	Inlet Gas	9,770 gmoles/min	2,310	----	----	-----	22.6
			Scrubber Spray	568 ℓ/min	-----	77.5	3.57	23.01	170.
		Outgoing Streams	Outlet Gas	10,800 gmoles/min	1,110	----	----	-----	12.0
			Downcomer	511 ℓ/min	-----	75.5	4.10	42.66	180.
			Scrubber Bottoms	57 ℓ/min	-----	74.7	4.07	40.37	19.6
				Σ Total S In = 192.6	Σ Total S Out = 211.6				
	Hold Tank	Incoming Streams	Scrubber Liquid	511 ℓ/min		71.0 72.9 73.3	3.66 4.22 4.19	31.02 34.39 35.31	166.
			Scrubber Bottoms	57 ℓ/min		53.3 58.5 80.6	5.10 4.72 2.76	29.14 28.56 29.07	18.2
			Clarifier Weir	45 ℓ/min		0.1		19.78	.9
		Outgoing Streams	Hold Tank Effluent	613 ℓ/min		80.2	3.60	23.45	191.4
				Σ Total S In = 185.1	Σ Total S Out = 191.4				
Set 2	Scrubber	Incoming Streams	Inlet Gas	9,770 gmoles/min	2,310				22.6
			Scrubber Spray	568 ℓ/min		83.0	3.53	23.21	179.
		Outgoing Streams	Outlet Gas	10,800 gmoles/min	1,110				12.0
			Downcomer	511 ℓ/min		81.3	4.34	42.13	201.5
			Scrubber Bottoms	57 ℓ/min		80.9	3.69	40.52	19.3
				Σ Total S In = 201.6	Σ Total S Out = 232.8				

TABLE 10.5-3 - TOTAL SULFUR MATERIAL BALANCE, EXPERIMENTS 1A AND 2A (cont.) Page 2

	Vessel		Stream Name	Stream Flow Rate	Total S in Gas (ppm)	Solids Content (g/ℓ)	Total S in Solids (mmoles/g)	Total S in Liquid (mmoles/ℓ)	Total S (gmoles/min)
RUN 1 Set 2 (cont.)	Hold Tank	Incoming Streams	Scrubber Liquid	511 ℓ/min		73.9 73.5 73.1	3.98 3.85 3.90	33.37 33.93 32.77	164.
			Scrubber Bottoms	57 ℓ/min		82.3 79.7 80.2	3.76 3.59 3.80	29.08 28.64 28.79	18.7
			Clarifier Weir	45 ℓ/min		0.3		19.47	8.8
		Outgoing Streams	Hold Tank Effluent	613 ℓ/min		79.7	3.49	27.37	186.8

Σ Total S In = 191.5 Σ Total S Out = 186.8

TABLE 10.5-4 - RATE CALCULATIONS USING LIQUID SPECIES BALANCES, EXPERIMENT 1A

Vessel	Reaction	Method of Calculation		Stream Name	Stream Flow Rate	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
RUN 1A								
Set 1 Marble Bed	$CaSO_3 \cdot \frac{1}{2}H_2O$ Precipitation	Gas/Liquid SO_2 Balance	Incoming Streams	Inlet Flue Gas	9,770 gmoles/min		2,310	22,600
				Scrubber Spray	568 ℓ/min	3.04		1,730
			Outgoing Streams	Outlet Flue Gas	10,800 gmoles/min		1,110	12,000
				Downcomer	511 ℓ/min	22.6		11,600
				Scrubber Bottoms	57 ℓ/min	23.8		1,350

$CaSO_3 \cdot \frac{1}{2}H_2O$ Precipitation Rate = Σ SO_2 (Liquid + Gas) In - Σ SO_2 (Liquid + Gas) Out - Oxidation Rate (assumed)

= 24,330 - 24,950 - .24 (22,600 - 12,000) = -3,160 moles/min

Vessel	Reaction	Method of Calculation		Stream Name	Stream Flow Rate	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
	$CaSO_4 \cdot 2H_2O$ Precipitation	Liquid SO_4 Balance + Oxidation Rate	Incoming Streams	Scrubber Spray	568 ℓ/min	20.0		11,3
			Outgoing Streams	Downcomer	511 ℓ/min	20.0		10,200
				Scrubber Bottoms	57 ℓ/min	16.6		946

$CaSO_4 \cdot 2H_2O$ Precipitation Rate = Σ SO_4 (Liquid) In - Σ SO_4 (Liquid) Out + Oxidation Rate

= 11,300 - 11,146 + .24 (10,600) = 2,694 mmoles/min

Vessel	Reaction	Method of Calculation		Stream Name	Stream Flow Rate	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
	$CaCO_3$ Dissolution	Liquid Ca Balance and Ca Precipitation Rates	Incoming Streams	Scrubber Spray	568 ℓ/min	19.1		10,800
			Outgoing Streams	Downcomer	511 ℓ/min	27.7		14,100
				Scrubber Bottoms	57 ℓ/min	26.9		1,530

$CaCO_3$ Dissolution Rate = Σ Ca (Liquid) Out - Σ Ca (Liquid) In + Σ Ca Precipitation Rates

= 15,630 - 10,800 + (-466) = 4,364 mmoles/min

Vessel	Reaction	Method of Calculation		Stream Name	Stream Flow Rate	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
Hold Tank	$CaSO_3 \cdot \frac{1}{2}H_2O$ Precipitation	Liquid SO_2 Balance	Incoming Streams	Scrubber Liuqid	511 ℓ/min	10.0		5,140
				Scrubber Bottoms	57 ℓ/min	7.18		409
				Clarifier Weir	45 ℓ/min	1.08		49
			Outgoing Streams	Hold Tank Effluent	613 ℓ/min	2.65		1,620

$CaSO_3 \cdot \frac{1}{2}H_2O$ Precipitation Rate = Σ SO_2 (Liquid) In - Σ SO_2 (Liquid) Out

= 5,598 - 1,620 = 3,978 mmoles/min

TABLE 10.5-4 - RATE CALCULATIONS USING LIQUID SPECIES BALANCES, EXPERIMENT 1A (cont.)

	Vessel	Reaction	Method of Calculation		Stream Name	Stream Flow Rate	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
RUN 1A									
Set 1 (cont)	Hold Tank (cont.)	$CaSO_4\cdot 2H_2O$ Precipitation	Liquid SO_4 Balance	Incoming Streams	Scrubber Liquid	511 ℓ/min	22.6		11,600
					Scrubber Bottoms	57 ℓ/min	21.7		1,240
					Clarifier Weir	45 ℓ/min	18.7		841
				Outgoing Streams	Hold Tank Effluent	613 ℓ/min	20.8		12,700

$CaSO_4\cdot 2H_2O$ **Precipitation Rate** = Σ SO_4 (Liquid) In - Σ SO_4 (Liquid) Out
= 13,681 - 12,700 = 981 mmoles/min

	Vessel	Reaction	Method of Calculation		Stream Name	Stream Flow Rate	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
		$CaCO_3$ Dissolution	Liquid Ca Balance and Cu Precipitation Rates	Incoming Streams	Scrubber Liquid	511 ℓ/min	24.3		12,400
					Scrubber Bottoms	57 ℓ/min	22.9		1,300
					Clarifier Weir	45 ℓ/min	17.9		807
				Outgoing Streams	Hold Tank Effluent	613 ℓ/min	19.4		11,900

$CaCO_3$ **Dissolution Rate** = Σ Ca (Liquid) Out - Σ Ca (Liquid) In + Σ Ca Precipitation Rate.
= 11,900 - 14,507 + 4,959 = 2,352 mmoles/min

	Vessel	Reaction	Method of Calculation		Stream Name	Stream Flow Rate	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
Set 2	Marble Bed	$CaSO_3\cdot \frac{1}{2}H_2O$ Precipitation	Gas/Liquid SO_2 Balance	Incoming Streams	Inlet Flue Gas	9,770 gmoles/min		2,310	22,600
					Scrubber Spray	568 ℓ/min	3.04*		1,730
					Outlet Flue Gas	10,800 gmoles/min		1,110	12,000
					Downcomer	511 ℓ/min	17.9		9,140
					Scrubber Bottoms	57 ℓ/min	16.2		924

$CaSO_3\cdot \frac{1}{2}H_2O$ **Precipitation Rate** = Σ SO_2 (Liquid + Gas) In - Σ SO_2 (Liquid + Gas) Out - Oxidation Rate (assumed)
= 24,330 - 22,064 - .24 (22,600 - 12,000) = -274 mmoles/min

	Vessel	Reaction	Method of Calculation		Stream Name	Stream Flow Rate	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
		$CaSO_4\cdot 2H_2O$ Precipitation	Liquid SO_4 Balance + Oxidation Rate	Incoming Streams	Scrubber Spray	568 ℓ/min	20.2		11,500
				Outgoing Streams	Downcomer	511 ℓ/min	24.2		12,400
					Scrubber Bottoms	57 ℓ/min	24.3		1,380

$CaSO_4\cdot 2H_2O$ Precipitation Rate = Σ SO_4 (Liquid) In - Σ SO_4 (Liquid) Out + Oxidation Rate
= 11,500 - 13,780 + .24 (10,600) = 260 mmoles/min

TABLE 10.5-4 - RATE CALCULATIONS USING LIQUID SPECIES BALANCES, EXPERIMENT 1A (cont.) Page 3

	Vessel	Reaction	Method of Calculation		Stream Name	Stream Flow Rate	Total Species in Liquid (mmoles/ℓ)	Total Species in Gas (ppm)	Total Species Flow Rate (mmoles/min)
RUN 1A Set 2 (cont.)	Marble Bed (cont.)	$CaCO_3$ Dissolution	Liquid Ca Balance and Cu Precipitation Rate	Incoming Streams	Scrubber Spray	568 ℓ/min	19.6		11,200
				Outgoing Streams	Downcomer	511 ℓ/min	30.0		15,300
					Scrubber Bottoms	57 ℓ/min	28.5		1,600
		$CaCO_3$ Dissolution Rate		= Σ Ca (Liquid) Out - Σ Ca (Liquid) In + Σ Ca Precipitation Rate = 16,900 - 11,200 + (-14) = 5,686 mmoles/min					
	Hold Tank	$CaSO_3 \cdot \frac{1}{2}H_2O$ Precipitation	Liquid SO_3 Balance	Incoming Streams	Scrubber Liquid	511 ℓ/min	10.3		5,260
					Scrubber Bottoms	57 ℓ/min	7.77		443
					Clarifier Weir	45 ℓ/min	1.12		50.4
				Outgoing Streams	Hold Tank Effluent	613 ℓ/min	12.47		7,640
		$CaSO_3 \cdot \frac{1}{2}H_2O$ Precipitation Rate		= Σ SO_3 (Liquid) In - Σ SO_3 (Liquid) Out = 5,753 - 7,640 = -1887 mmoles/min					
		$CaSO_4 \cdot 2H_2O$ Precipitation	Liquid SO_4 Balance	Incoming Streams	Scrubber Liquid	511 ℓ/min	22.9		11,700
					Scrubber Bottoms	57 ℓ/min	20.8		1,190
					Clarifier Weir	47 ℓ/min	18.3		823
				Outgoing Streams	Hold Tank Effluent	613 ℓ/min	14.9		9,130
		$CaSO_4 \cdot 2H_2O$ Precipitation Rate		= Σ SO_4 (Liquid) In - Σ SO_4 (Liquid) Out = 13,713 - 9,130 = 4,583 mmoles/min					
		$CaCO_3$ Dissolution	Liquid Ca Balance and Cu Precipitation Rates	Incoming Streams	Scrubber Liquid	511 ℓ/min	24.5		12,500
					Scrubber Bottoms	57 ℓ/min	21.7		1,240
					Clarifier Weir	45 ℓ/min	17.6		792
				Outgoing Streams	Hold Tank Effluent	615 ℓ/min	24.8		15,200
		$CaCO_3$ Dissolution Rate		= Σ Ca (Liquid) Out - Σ Ca (Liquid) In + Σ Ca Precipitation Rate = 15,200 - 14,530 + 2,690 = 3,360 mmoles/min					